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DEVELOPMENT AND OPTIMIZATION OF PYRRONE POLYMERS

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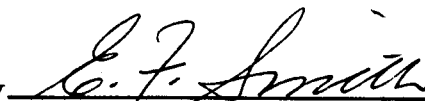
HUGHES AIRCRAFT COMPANY
CULVER CITY, CALIFORNIA

DEVELOPMENT AND OPTIMIZATION OF
PYRRONE POLYMERS

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Approved by



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AEROSPACE GROUP

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ABSTRACT

This report describes the development and optimization of Pyrrone polymers, that is, those polymers formed from the condensation reaction of aromatic dianhydrides with aromatic tetraamines in various solvents.

The work was divided into two consecutive phases based upon both the type of dianhydride used and the solvent media in which the reactions were conducted.

In Phase I, the primary efforts were directed towards the synthesis and characterization of the polymer formed from the condensation of pyromellitic dianhydride (PMDA) with diaminobenzidine (DAB) in polar solvents, and the subsequent preparation and testing of fabricated articles. The resultant polymer gave disappointing strength properties; these were attributed to the poor flow characteristics inherent in the polymer-solvent system.

In Phase II, primary efforts were directed toward the synthesis, characterization, and subsequent fabrication of the polymer formed from the condensation of benzophenone tetracarboxylic dianhydride (BTDA) with diaminobenzidine (DAB) in the esterifying solvent ethylene glycol (EG). Fiberglass laminates formed with the Phase II polymer had room temperature flexural strengths above 70,000 psi and moduli on the order of 5×10^6 psi. This improvement is attributed to several factors including the elimination of the ionic interaction between the polymer and polar solvents, the plasticizing effect of internally bound ethylene glycol, and the inherent increased flexibility of the additional BTDA single bond. Pyrrone polymers synthesized in ethylene glycol are tractable and laminates based on these polymers show promise as a high temperature resistant structural material.

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1.0 INTRODUCTION

Pyrrones, a new class of polymers developed at the NASA Langley Research Center, offer promise in present and future aerospace applications. The ladder-like structures of the aromatic heterocyclic polymers have a greater proportion of aromatic cyclic groups than any other developmental polymer.

Pyrrones may be formed from many cyclic dianhydrides and tetraamines under comparatively simple reaction conditions. Depending upon the starting materials used, two basic structures are obtained: the stepladder and the ladder polymers. In the stepladder form, the polyaromatic moieties are linked by single bonds. The ladder Pyrrone is linked by double bonds at each end of the basic Pyrrone unit to form a continuous double strand polymer.

During the first year of this program many of the unsuspected complexities in the development and optimization of this class of materials have been uncovered. This summary presentation of the first year's technical efforts has been divided into two phases.

Phase I involves investigations primarily concerned with the synthesis of a Pyrrone polymer in polar solvents, the characterization of this polymer system, and the development and optimization of techniques conducive to the fabrication of laminated parts. The coating, adhesive and dielectric properties of this polymer system also were investigated. In Phase I most of the effort was concentrated on a polymer system consisting of the condensation products of pyromellitic dianhydride (PMDA) and diaminobenzidine (DAB) in either dimethylacetamide (DMAc), dimethylformamide (DMF) or N-methyl pyrrolidone (NMP).

The physical properties of laminated parts made from the Phase I polymer systems indicated that high strengths probably would not be achieved with the polymer system in its present form due to the poor flow and molding characteristics inherent in the system. For this reason, the problem was circumvented by initiating Phase II of the program in which the polymer and solvent systems were changed.

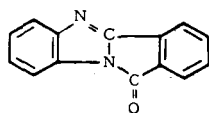
In Phase II the basic polymer system consisted of the condensation products of benzophenone tetracarboxylic dianhydride (BTDA) and diaminobenzidine (DAB) in ethylene glycol (EG). This system is a stepladder type Pyrrone because of the single bonds in both the BTDA and DAB molecules. In addition to the inherent increased molecular flexibility of this stepladder type polymer and the elimination of ionic interaction between polymer and solvent, the ethylene glycol appears to be bound chemically to the dianhydride in the polymer to give a molecular "plasticization." The expected increase in resin flow characteristics due to the increased polymer chain flexibility and internally bound solvent was indeed realized, since the strength values obtained from the Phase II polymer systems are approximately double those obtained for similar laminated parts in Phase I of the program.

2.0 PHASE I STUDIES

The evaluation of the materials produced in Phase I of the program was based upon the chemical behavior (Sections 2.1 and 2.2), characterization of the resins (Section 2.3), and the physical properties obtained on laminates, moldings, coatings and precipitated powders (Sections 2.4 through 2.8). The conclusions drawn from this investigation are presented in Section 2.9.

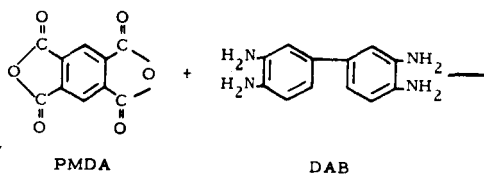
2.1 GENERALIZED REACTIONS

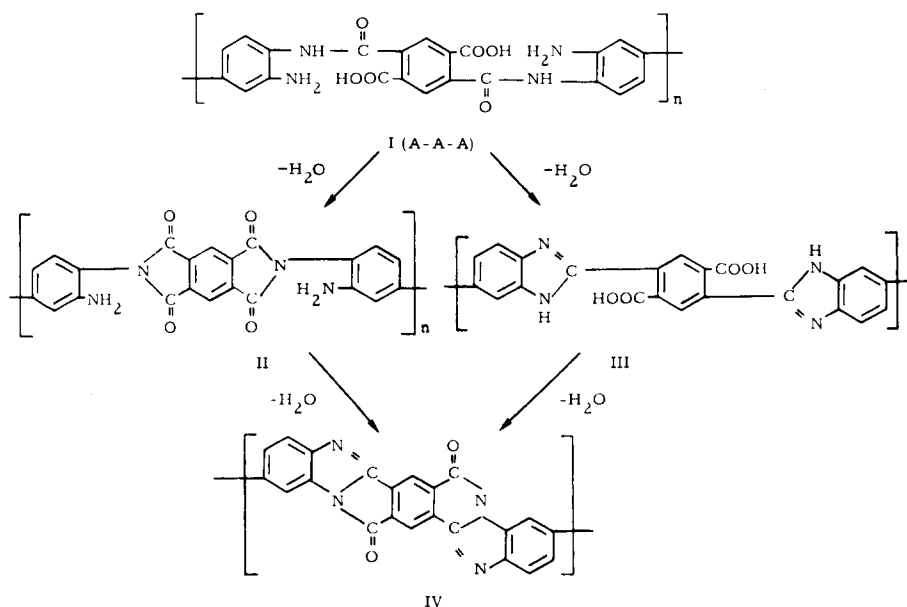
The Pyrrones are a class of heterocyclic aromatic polymers having the following moiety as a recurring unit in the polymer chain:



This type of polymer was prepared first by Pezdirtz and Bell² under the name polyimidazopyrrolones²⁻⁴ or Pyrrones. Other pioneers in this field referred to these polymers as polybenzimidazolimides⁵ or polybenzoylenebenzimidazoles.⁶

Pyrrones generally have been synthesized by the reaction of aromatic dianhydrides with aromatic tetraamines. The reactions are illustrated by the typical equations shown below for pyromellitic dianhydride (PMDA) and 3,3'-diaminobenzidine (DAB).



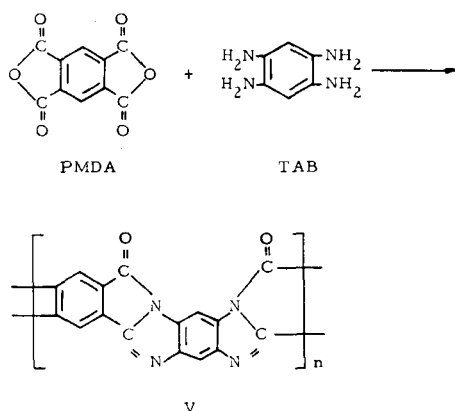


Several isomeric structures are possible for each of the indicated types of polymers. The initial reaction product (I) is a polyamide which undergoes two successive condensation reactions to form the Pyrrone (IV). Two main routes to the fully cyclized polymer are possible. Colson, Michel and Paufler⁶ found that the preferred route at temperatures between 130 - 150°C led to the formation of the polyimide (II), while others^{3,5} found evidence for the involvement of both polyimide and polybenzimidazole (III) intermediates.

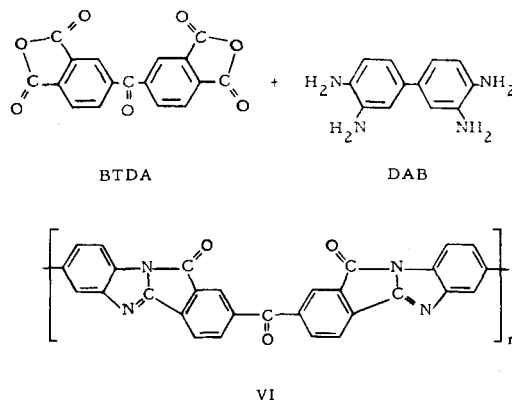
Although the Pyrrone (IV) is insoluble, the amino-acid-amide (A-A-A) polymer (I) dissolves readily in such solvents as N,N-dimethylacetamide (DMAc) and N,N-dimethylformamide (DMF), from which strong, but brittle, films can be cast. Cyclocondensation to convert (I) to (II) occurs at about 130 to 150°C in a film, and further condensation to form IV takes place above 200°C, with temperatures as high as 250°C required for complete conversion.⁶

One reason for the interest in Pyrrones is the possibility of forming ladder polymers, which theoretically should possess a considerable advantage over single-stranded polymers in terms of stability to

radiation and heat. Such a ladder polymer can be formed, for example, from pyromellitic dianhydride (PMDA) and 1, 2, 4, 5-tetraaminobenzene (TAB).^{2, 3, 5, 6}



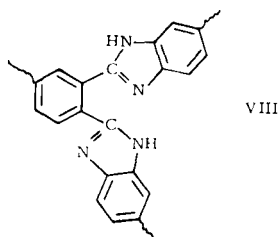
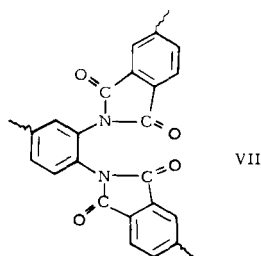
Most of the known Pyrrone polymers, however, have only a partial ladder structure and have been dubbed "stepladder" polymers.¹⁻³ These polymers are exemplified by polymers (IV) and (VI), the latter being derived from 3,3', 4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and DAB.



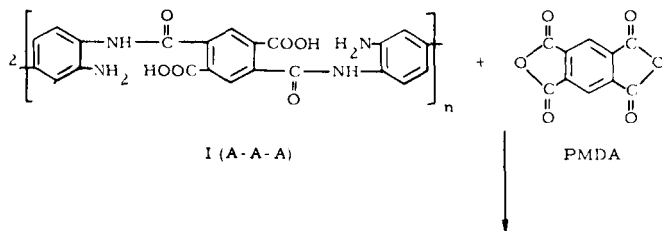
Ladder polymer (V), because of its stiff, double-stranded chain, is less soluble than the stepladder polymers.⁵ It seemed judicious, therefore, to concentrate the efforts of this program on readily fabricated polymers (IV) and (VI), in spite of their somewhat lower inherent stability to heat and radiation.

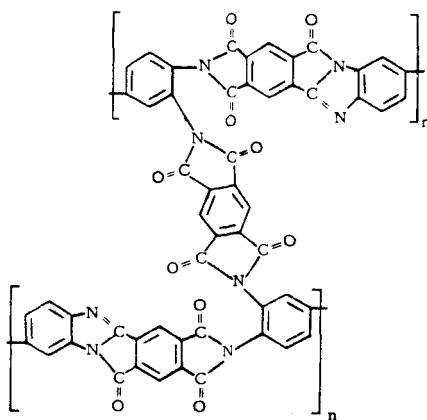
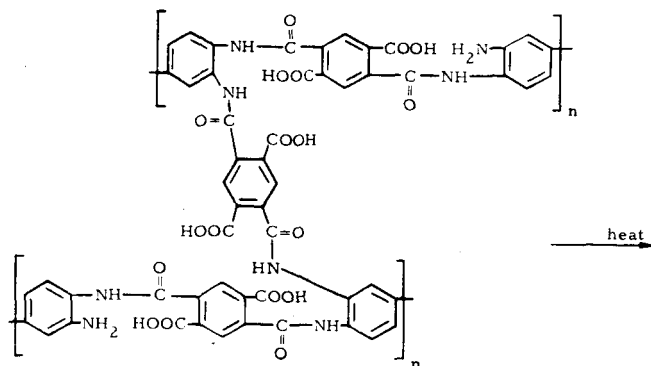
The nature and extent of crosslinking also may have a significant effect on the properties of the cured product. Simple crosslinks

probably do not exist to a great extent, but a three-dimensional polymer can result from extensive branching. Two types of stable branching seem likely to be present, one involving imide linkages (VII) and the other having imidazole groups (VIII).



Gelation of the A-A-A polymer (I) occurs quickly in solution when a slight excess of dianhydride is added, but not when an excess of tetraamine is present.⁶ Amide crosslinks (as shown in IX) are the cause of this gelatin, since the amide groups are formed only with anhydride and not with the much less reactive carboxyl groups. These crosslinks would appear to be conducive to the formation of imide branches or crosslinks of the type shown in (VII) and (X).

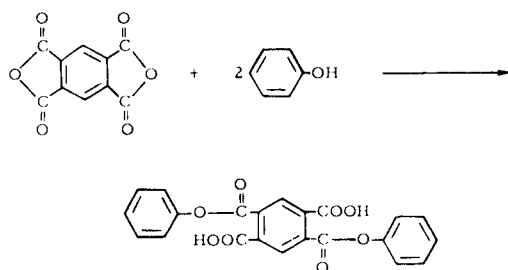




Using phthalic anhydride and *o*-phenylenediamine as model compounds, however, Dawans and Marvel⁵ found a tendency to form branches of the type indicated by (VIII) and reported none of the type shown in (VII).

Pyrrone polymerizations have been carried out both in a melt and in solution. Preferred solvents have been DMAc, DMF, dimethyl sulfoxide (DMSO), and polyphosphoric acid, but bis (2-methoxyethyl) ether (diglyme), phenol, and pyridine have also been used. Strong bonding between the polymer and the solvent^{2, 3} as well as between the polymer and moisture from the air,⁴ has been noted. Interaction between the monomers and certain solvents is also likely. This program has revealed that the solvent can exert an extremely important effect on the strength of the formed and cured composite.

With few exceptions, the monomers always have been the dianhydride and the tetraamine or the tetraamine tetrahydrochloride. Bell and Jewell⁴ have reported using 2,5-dicarbomethoxyterephthaloyl chloride in place of PMDA with no apparent change in polymer properties. Free tetracarboxylic acids were reacted with tetraamines to prepare polybenzimidazobenzophenanthrolines,^{8,9} a class of polymer which is related structurally to the Pyrroles. Pyrrole synthesis in phenol⁵ almost certainly proceeded in part through phenyl ester intermediates, although this was not specifically mentioned in the report.



A prior interaction between the monomers and other solvents is conceivable also, and such reactions would make the actual monomers something other than the initial dianhydrides and tetraamines.

The efforts on this program logically fall into two phases. In the first phase DMAc, DMF and other presumably unreactive solvents were employed as the medium for the synthesis of the A-A-A polymer. In the second phase ethylene glycol served as the solvent, and the anhydrides were intentionally converted to esters prior to reaction with the tetraamine. These two phases of the program are discussed separately in this report.

2.2 SYNTHETIC ROUTES

Establishment of satisfactory reaction conditions to prepare developmental quantities of Pyrrole polymers from PMDA and DAB and from BTDA and DAB was the objective of the synthesis effort. In general, the experimental approach of Phase I followed procedures developed by Bell and Pezdirtz^{2,3} quite closely.

Most of the experimental resins were prepared from PMDA and DAB in DMAc. Commercial PMDA was sublimed in 2-pound batches prior to use, and the DAB was used as received. DMAc was carefully dried for some experiments, although commercial technical grade at first was considered to be satisfactory without further purification and large quantities of resin were prepared in this unpurified solvent.

The reactions were carried out by adding a solution of the anhydride to a vigorously stirred solution of the tetraamine in a Waring blender. The apparatus was contained in a polyethylene bag which alternately was evacuated and flushed with argon to displace the air prior to the start of the reaction.

A few small-scale experiments were performed first in a very small Waring blender to develop suitable methods for handling the reaction. In these preparations 95 percent of the theoretical quantity of PMDA was added to the DAB in one portion, and additional PMDA solution then was added dropwise until a desired viscosity was achieved. It was noted, however, that gel particles formed within seconds after only the first portion of PMDA solution was added, regardless of the rate of addition. This premature gelation was attributed to local excesses of PMDA in the mixture which resulted from inadequate stirring in the small size blender. When the reaction was conducted in a larger blender, which provided more rapid mixing, gelation was virtually eliminated until an excess of PMDA was present.

Samples of the reaction mixture were drawn up into a tube periodically, and the viscosity was determined by measuring the time required for a steel ball to drop through a given column of solution. Figure 1 shows a plot of the drop time for the steel ball as a function of the number of drops of PMDA solution added after the initial 95 percent of the theoretical amount of PMDA had been combined with the DAB. As can be seen from the shape of the curve in Figure 1, the appropriate end point was not obvious, and no sudden changes in viscosity occurred.

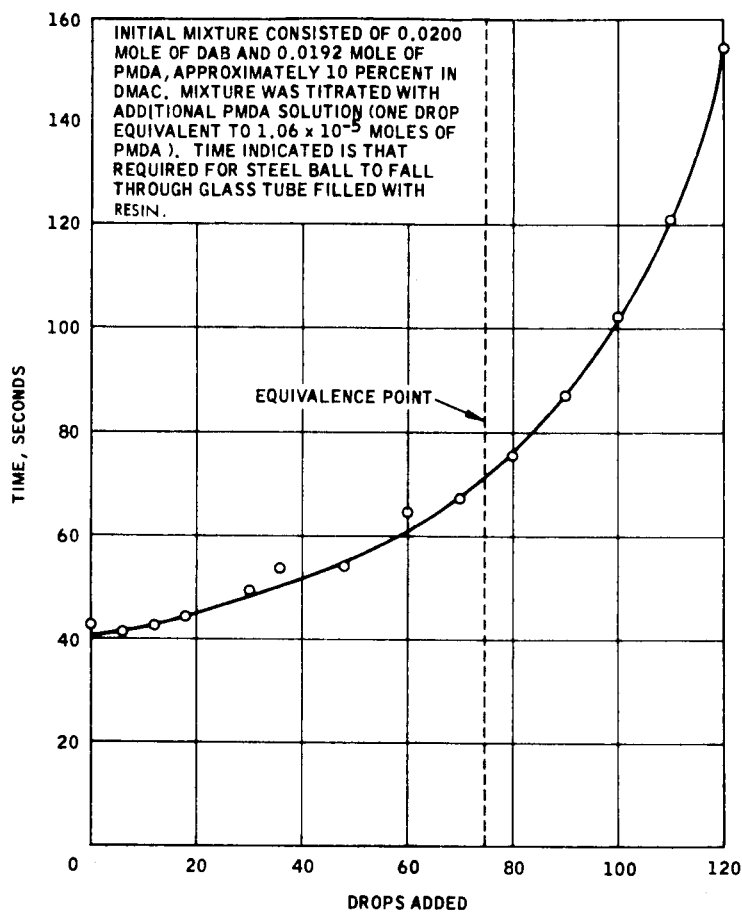


Figure 1. Viscosity Curve of PMDA-DAB Pyrrone Resin Near Endpoint of Reaction

The reaction was exothermic, and the heat of reaction plus the heat introduced by stirring quickly raised the temperature from ambient to about 55°C. Efficient cooling methods appeared desirable.

After the initial experiments the preparation was scaled up and run in a one-gallon Waring blender equipped with a water-cooled base and an internal cooling coil. A large water bath controlled at 25°C was used as a source of cooling water. Excessive cooling seemed to slow the reaction to an undesirable extent, however, and after two runs with efficient cooling it was decided to allow the temperature to rise as high as 50°C. The higher temperature was important particularly when the viscosity of the solution was used to indicate the end point of PMDA addition. If this end point was determined at 25°C, the amount of PMDA added was actually an excess, and the resin gelled subsequently during storage. However, if this end point was determined at 50°C, the reaction essentially was complete at the time of titration, and the excess of dianhydride and the resulting gelation were avoided.

Gel formation was minimal in the one-gallon container. In one instance the gel was isolated by filtration, dried, weighed and found to comprise 0.27 percent of the solids by weight. This gel was produced from a reaction of equivalent molar quantities of PMDA and DAB.

In all cases, the resins did not have the same viscosity even when the preparative methods seemed to differ only in unimportant details. A pH value was determined occasionally for the resulting resin, although the significance of a pH measurement in DMAc is not certain. These pH values also varied considerably, falling in the range between 3.9 and 5.5.

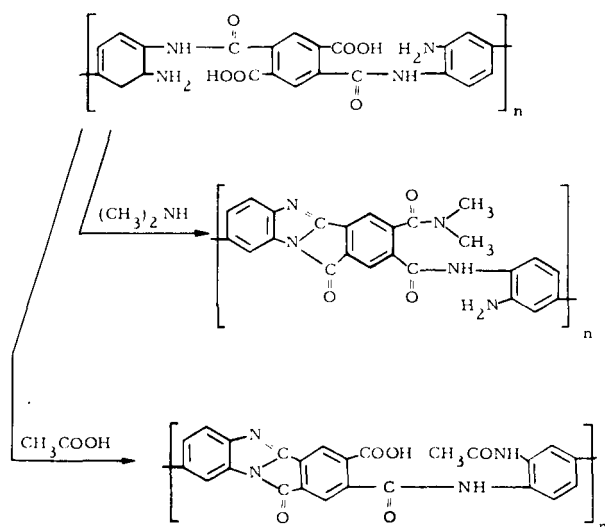
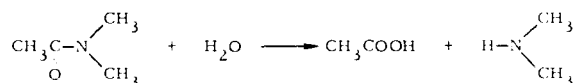
Since the viscosity did not indicate a sharp end point, the concept of titrating to a viscosity end point with the last portion of PMDA solution was abandoned. Subsequently PMDA and DAB were combined in equal molar proportions.

Following several exploratory preparations in the one-gallon blender, a series of preparations was undertaken to provide a 10-gallon master batch of resin (J-1). The viscosity of the J-1 resin was determined at various temperatures using a Brookfield LVF 1 at 60 rpm —

number two spindle. The results are shown in Figure 2 which depicts a typical viscosity temperature curve.

The resulting resins were blended in a storage tank, then concentrated by evaporation in a rotary still to a calculated solids content of 20.4 percent. J-1 resin had an intrinsic viscosity of 0.41. The pH of the DMAc solution was 3.9, the lowest of the pH values measured.

The low flexural strength of laminates fabricated from resin J-1 was a disappointment (see Section 2.4). In part this could be attributed to the poor flow properties of the resin. However, an odor of acetic acid was always present when the resin was processed, suggesting that substantial quantities of solvent (DMAc) remained strongly bound to or trapped in the resin during cure, and that this solvent hydrolyzed to yield acetic acid. Water for the hydrolysis could be furnished by the cyclocondensation of the polymer. The possibility existed, therefore, that the bound solvent was responsible for poor polymer properties. This bound solvent increased the void content of the cured products. Moreover, chemical reactions of the following type might occur:



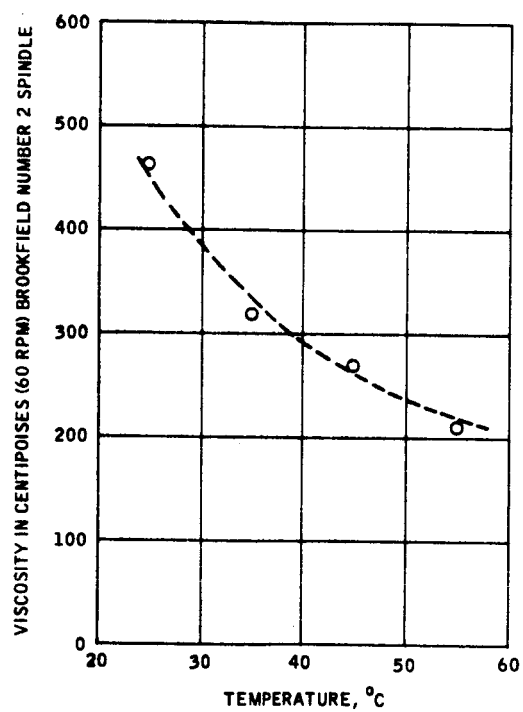


Figure 2. Viscosity of J-1 Resin
as Function of
Temperature

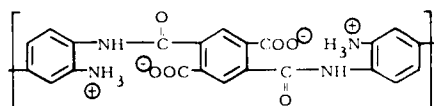
Some of the reaction products may inhibit or prevent the curing reactions.

In response to these developments, two new approaches were undertaken. First, both reagent grade and technical grade DMAc were purified further by distillation from phosphorus pentoxide and treatment with a molecular sieve. Resins were prepared in the purified solvents and were used to prepare test specimens. The odor of acetic acid was no longer detected during the fabricating operation and the finished parts were superior in appearance to previous laminates, but the flexural strengths were scarcely altered. Polymers with slightly lower intrinsic viscosities were obtained in the purified DMAc than in the technical grade solvent.

The second approach was to eliminate DMAc entirely and use DMF and N-methyl-2-pyrrolidone (NMP) as the solvent. Spectrographic grade DMF was dried on a molecular sieve column prior to use. Technical grade NMP was fractionated, then distilled from phosphorus pentoxide and passed through the molecular sieve column. Resins were prepared in these solvents by essentially the same procedure used for the DMAc resins.

Portions of polymer were precipitated from the DMAc resins with water and acetone. Precipitation with water was unsatisfactory because the polymer retained a substantial quantity of residual DMAc. The polymer precipitated with acetone was an infusible, fine yellow powder which turned light green in air and which was readily resolvable in DMAc, DMF, NMP, and DMSO. These polymer samples were used for differential thermal analyses and for molding specimens of pure resin.

Resins with only a 2-percent concentration of solids were also prepared in purified DMAc and tested because it was recognized that the A-A-A polymer has a zwitterionic structure (XI) rather than the nonionized structure (I). The ionic character of the polymer



XI

produces strong intermolecular attractions which may cause the polymer molecules to be closely associated in concentrated solutions. Closely associated polymer molecules may undergo branching reactions during the polymer preparation, and the branches may inhibit complete cyclization to the Pyrrone structure. To minimize this possible tendency toward branching, the polymer was prepared in a more dilute solution in which the polymer molecules should be more isolated from each other. Polymers prepared in dilute solutions had lower intrinsic viscosities, but after concentration of the resin and fabrication of laminates, the final products were essentially the same as those derived from concentrated solutions.

A Pyrrone resin sample also was prepared from BTDA and DAB in DMAc. The procedure was similar to that for the PMDA-DAB syntheses.

2.3 CHARACTERIZATION OF RESINS

As work progressed throughout Phase I of the program it became apparent that the PMDA-DAB resins in the polar solvents (DMAc, DMF and NMP) could not be expected to produce laminates with flexural strengths much better than 40,000 psi and moduli much over 3 million psi. Since appropriate fabrication techniques were used, it is believed that the reason for the formation of mediocre laminates was in the basic resin system rather than in the laminating techniques. Some of the latter laminates prepared toward the end of Phase I were made with resins that were synthesized in highly purified and carefully dried solvent, but no marked improvements in physical properties were evident. The presence of impurities in the solvents, although detrimental, was not the prime reason for the comparatively low physical properties. If the polymers were not sufficiently solvated, i.e., the solubility of the polymer in the resin solvent was poor, this would be indicated by intrinsic viscosity data. With this in mind, a series of intrinsic viscosity measurements was conducted on the resins that had been synthesized in the different types of solvents.

Intrinsic Viscosity

Reduced viscosity versus concentration data was developed for a series of the resins synthesized in Phase I of the program. The intrinsic viscosities of each of these systems were determined from the experimental data by applying the relationship

$$[\eta] = \left(\frac{\eta_{sp}}{C} \right)_{C=0}$$

where $[\eta]$ is the intrinsic viscosity and $(\eta_{sp}/C)_{C=0}$ is the reduced viscosity versus concentration plot extrapolated to zero concentration. The viscosity data were obtained for the resins prepared in various solvent systems. All viscosity data were developed with an Ostwald-Fenske viscometer at a constant 25°C temperature.

The following information was obtained by examination of the intrinsic viscosity data and the shape of the reduced viscosity versus concentration curves. Both polymers which were synthesized in dried reagent grade solvents exhibited curves typical of polyelectrolytes in solution. As the resins were diluted to lower concentrations (below 0.2 gram/100 ml) the curves rose rapidly and appeared to be approaching the zero concentration axis asymptotically. This behavior was drastically reversed in the case of the acidified resin which exhibited the highest intrinsic viscosity yet had the low concentration portion of the curve approaching the origin. This increased intrinsic viscosity upon addition of the electrolyte (HCl) indicates that the increased concentration of anionic and cationic counter-ions tends to suppress the formation of an infinite network. Those polymers synthesized in purified technical grade solvents exhibited behavior similar to that of the acidified resin except that lower intrinsic viscosities were obtained. This appears to indicate that the "purified" solvents contained enough impurities to act as counter-ions in suppressing gel formation but were still relatively poor solvents. The relatively low intrinsic viscosities of the cold run and dilute runs were probably due to a combined effect involving both counter-ions plus lower molecular weights as a result of a low degree of polymerization caused by low temperatures and dilution.

Dynamic Modulus

It was found feasible to coat a 3/32-inch diameter cylindrical steel rod with Pyrrone resin for dynamic modulus measurements. Previous attempts to coat thin beryllium-copper strips with the Pyrrone resin were unsuccessful since cracking of the resultant film always occurred at sharp corners during drying. One steel rod was given eight coatings with NASA Pyrrone resin No. M-11 which gave an average film thickness of 5-6 mils. At this point, the remainder of the M-11 resin gelled completely preventing further coating.

Vibrating Reed Analysis of a high solids (~50 percent) J-1 Pyrrone resin in DMAc was undertaken. A three-ply laminate of E glass and Pyrrone, previously cured out at 1000 psi at 600°F, was employed as the supporting substrate. A 1/2 x 3-inch strip of substrate was subjected to a temperature cycle of 75-500°F. The apparent modulus E_{app} was found to be linear with temperature.

The inert substrate was coated with a high solids Pyrrone resin (concentrated by vacuum evaporation at room temperature) and its apparent dynamic modulus monitored. The coating was approximately 6 mils thick and adhered well to the substrate. The temperature was held at 100°C during the cure phase of the investigation. The resin became glassy and the modulus remained constant after approximately 110 minutes.

The temperature controller was set at 270°C and both heating elements activated. The temperature rose from 100 to 270°C in 40 minutes. During this period the relative modulus was observed at selected temperatures.

At a constant temperature of 100°C, the first 75 minutes of cure are a combination of solvent removal and some condensation reaction. From 75 minutes to about 110 minutes it appears that the change of modulus is due principally to further condensation of acid-amino groups. At about 110 minutes the resin is in a glassy state thus preventing any main chain crankshaft rotation. Restriction of this mode of rotation prevents further condensation from occurring. It is probable

that the restriction to main chain rotation is due to intermolecular forces which are abundantly present in the A-A-A polymer and perhaps to some three dimensional crosslinking.

When the change of relative modulus with temperature is plotted, the initial section of the curve is linear with temperature thus yielding a constant dE_{rel}/dT up to 175°C. At this temperature a sudden jump in modulus is observed which is apparently associated with the condensation to the amine-imide. At about 210-215°C an additional modulus increase is observed that is indicative of further condensation to the Pyrrone structure.

Stainless steel substrates were coated with J-1 resin and PMDA-DAB resin synthesized in DMAc. One of the coated substrates was used in an effort to determine the relative dynamic modulus of the polymer as a function of temperature. The coated substrate was heated from ambient to 300°C while monitoring the fundamental frequency of vibration. No appreciable change in modulus was detected.

2.4 LAMINATING AND PHYSICAL PROPERTIES

Criteria for the development of satisfactory Pyrrone laminates were the flexural strength and modulus that could be achieved with a particular resin system. Once a resin system showed promise as a laminating material, it was tested further to see if it were also a high temperature stable material. The results of these laminating studies for Phase I of the program are summarized in Tables I and II.

The first laminates recorded are the PF-14 series. The earlier series of laminates were part of a familiarization program; thus, no significant results were obtained for laminates PF-1 through PF-13. These laminates were formed using several resins submitted by NASA Langley (designated N-4 and M-11) plus several experimental resins synthesized at Hughes.

Examination of Table I indicates that all laminates were formed using a standard reinforcement (with the exception of PF-21 where CCA-1 carbon cloth was used). The standard reinforcement selected

Laminate Designation (1) (2)	Laminating Conditions		Final Resin Content, percent	Density, gm/cc	Volume Percent Voids in Resin, percent	Average Flexural Strength (psi x 10 ⁻³)		Average Modulus (psi x 10 ⁻⁶)		Remarks
	Contact Time, minutes	Maximum Pressure, psi	Maximum Temp., °F			Room Temp.	Elevated Temp. (At 600°F after 1/2 hr. at 600°F)	Room Temp.	Elevated Temp. (At 600°F after 1/2 hr. at 600°F)	
PF14-1 ⁽³⁾	0	500	200	-	-	16.7	-	1.29	-	-
PF14-2 ⁽³⁾	0	500	300	-	-	21.8	-	1.42	-	-
PF14-3 ⁽³⁾	0	500	400	-	-	23.1	-	1.44	-	-
PF14-4 ⁽³⁾	0	500	500	-	-	16.1	-	1.35	-	-
PF14-5 ⁽³⁾	0	500	600	-	-	16.6	-	1.38	-	-
PF15-1	-	50	600	15.8	1.59	37.0	22.1	1.74	1.52	Laminate formed by vacuum bag technique
PF15-2	-	50	600	15.8	1.56	34.0	18.9	1.66	1.35	Laminate formed by vacuum bag technique
PF16-1	5	2000	600	25.0	1.56	37.0	-	1.66	-	-
PF16-1A ⁽⁴⁾	5	2000	600	25.0	1.56	11.7	-	1.49	-	-
PF16-2	5	5000	700	24.0	1.70	32.9	-	2.24	-	-
PF17	0	1000	750	30.5	1.82	39.7	-	2.29	-	-
PF18-1	0	500	650	23.0	1.52	29.1	-	1.91	-	No elevated temp. testing was conducted
PF18-2	0	500	700	24.0	1.54	28.7	-	2.07	-	No elevated temp. testing was conducted
PF18-3	0	500	750	23.0	1.50	27.9	-	1.96	-	No elevated temp. testing was conducted
PF18-4	0	2500	650	25.0	1.66	29.5	-	2.14	-	No elevated temp. testing was conducted
PF18-5	0	2500	700	23.0	1.72	31.6	-	2.30	-	No elevated temp. testing was conducted
PF18-6	0	2500	750	24.0	1.71	34.9	-	2.49	-	No elevated temp. testing was conducted
PF18-7	0	5000	650	25.0	1.70	30.5	-	1.93	-	No elevated temp. testing was conducted
PF18-8	0	5000	700	23.0	1.74	29.9	-	2.11	-	No elevated temp. testing was conducted
PF18-9	0	5000	750	23.0	1.80	36.7	-	2.69	-	No elevated temp. testing was conducted
PF19	-	200	350	-	-	-	-	-	-	Laminate formed by vacuum bag technique
PF20	0	500	600	-	-	41.0	-	3.10	-	No elevated temp. testing was conducted
PF21 ⁽⁵⁾	0	1300	600	-	-	10.6	-	1.37	-	No elevated temp. testing was conducted

(1) All PMDA-DAB resins were in DMAC solvent

(2) All laminates were fabricated using style 181 "E" glass cloth with an A-1100 finish with the exception of PF-21

(3) Laminates PF-14-1, 2, 3, 4, 5 were postcured at 600°F for 2 hours in air

(4) Laminate PF-16-1A was postcured at 600°F for 72 hours in air

(5) Laminate PF-21 was fabricated with CCA-1 carbon cloth reinforcement

Table I Summary of PMDA-DAB-DMAC Laminate Properties for Phase I Program

Laminate Designation (1)	Resin Designation	Laminating Conditions		Final Resin Content, Percent	Density, gm/cc	Volume Percent Voids in Resin	Average Flexural Strength (psi x 10 ⁻³)		Average Modulus (psi x 10 ⁻⁶)		Remarks
		Contact Time, minutes	Maximum Pressure, psi	Maximum Temp., °F			Room Temp.	Elevated Temp. (At 600°F after 1/2 hr. at 600°F)	Room Temp.	Elevated Temp. (At 600°F after 1/2 hr. at 600°F)	
PF22-1	J-1 ⁽²⁾	3/4	1000	300	34.4	—	40.5	—	3.13	—	No elevated temp. testing was conducted
PF22-2	J-1 ⁽²⁾	0	1000	300	—	—	34.1	—	2.79	—	No elevated temp. testing was conducted
PF23	J-1 ⁽²⁾	0	1000	900	16.5	—	—	—	—	—	Laminate blew apart due to excessive outgassing
PF24	NASA ⁽²⁾	0	200	600	26.3	1.46	25.0	19.5	2.19	1.75	—
PF25	NASA ⁽²⁾	5	200	600	—	—	—	—	—	—	No laminate was formed resin "washed out"
PF26	D1516-29Y ⁽²⁾	4	200	600	18.3	1.52	32.9	24.7	3.14	2.65	—
PF27	D1516-29X ⁽²⁾	3	200	600	20.5	1.54	33.8	26.4	3.12	2.74	—
PF28	D1516-29Z ⁽²⁾	2-1/2	200	600	15.8	1.54	41.7	33.7	2.90	2.70	—
PF29	Narmco ⁽²⁾	1/2	1000	600	13.6	1.58	33.0	24.0	3.09	3.09	—
PF30	Narmco ⁽²⁾	1/3	1000	600	11.1	1.52	18.9	22.0	3.09	2.97	—
PF31	Narmco ⁽²⁾	1/3	1000	600	16.7	1.56	34.7	26.0	3.22	3.00	—
PF32	Narmco ⁽²⁾	1/3	1000	600	11.8	1.58	30.5	25.2	3.81	3.38	—
PF33	Narmco ⁽²⁾	1/3	1000	600	15.5	1.52	36.1	24.9	3.70	3.13	—
PF34	D1516-30X ⁽³⁾	1/3	1000	600	17.2	1.62	36.4	30.1	3.64	3.36	—
PF36	D1516-34R ⁽²⁾	3-1/2	1000	600	4.2	—	—	—	—	—	Delaminated during trimming
PF38	D1516-33 ⁽⁴⁾	1/2	1000	600	21.8	1.51	44.4	29.7	3.13	2.81	—
PF39	D1516-31X ⁽⁵⁾	1	1000	600	18.3	1.53	38.4	26.5	2.71	2.03	—
PF40	D1516-29X ⁽²⁾	—	100	600	16.4	1.55	30.7	21.7	3.08	2.77	Laminate formed by vacuum bag technique

(1) All laminates were fabricated using Style 181 "E" glass cloth with an A-1100 finish

(2) PMDA-DAB resins in DMAC solvent

(3) PMDA-DAB resin in DMF solvent

(4) BTDA-DAB resin in DMAC solvent

(5) PMDA-DAB resin in NMP solvent

Table II Summary of PMDA-DAB and BTDA-DAB Laminate Properties for Phase I Program

for the lamination studies was 181 glass cloth with an A1100 finish. By using a standard reinforcement material, this variable could be controlled until the time that optimization of the reinforcement was desired.

All resins used in Phase I were of the PMDA-DAB-polar solvent type except the resin used to prepare laminate PF-38, which was of the BTDA-DAB type in N,N, dimethylacetamide (DMAc). The various PMDA-DAB resins were in one of three solvents, DMAc, N-methyl-2-pyrrolidone (NMP) or N,N, dimethylformamide (DMF). The majority of resins and subsequent laminates were made with the PMDA-DAB system in DMAc. The initial work used a Hughes synthesized PMDA-DAB-DMAc resin designated J-1. Laminates PF-14 through PF-24 were formed with this resin system. Many conditions were attempted using this resin system. The pressures applied to the laminates were varied from 50 to 5000 psi with the best strength values obtained in the intermediate pressure ranges (i. e. , 200 to 1000 psi). This indicated that with the resin systems in polar solvents, a moderate amount of pressure was necessary to achieve resin flow during the laminating operation. Pressure alone was not responsible for obtaining optimum strength because the laminating temperature was varied along with the pressure in many instances. In almost all cases the laminates cured at the higher temperatures achieved the best strengths.

There is a rule of thumb (with few exceptions), that those conditions of time, temperature, and pressure necessary to obtain laminates with optimum resin contents, densities, and low voids, also result in laminates with the highest flexural strengths and moduli.

To better illustrate the complexities in attempting to optimize the PMDA-DAB-DMAc system, the operations that were followed in the formation of the various laminates are discussed in the following sections.

Hughes J-1 Resin

Five laminates were formed at 500 psi pressure with the press temperature varied from 200 to 600°F at 100°F intervals. The five laminates were postcured for 2 hours at 600°F in air. The laminate with the best strength properties was PF-14-3 that was pressed at 400°F and postcured 2 hours at 600°F in air.

Two vacuum bagged laminates were formed at 50 psi pressure and at a maximum press temperature of 600°F. These vacuum bagged laminates had much higher strength properties than those formed at 500 psi pressure.

Three laminates were formed to determine the effect variable pressures and temperatures on the properties of laminates formed with J-1 resin. The highest strengths were achieved at 750°F press temperatures while the effect of pressure was not clearly defined since both a 1000 psi laminate (PF-17) and a 5000 psi laminate (PF-18-9) showed comparable flexural strengths.

A laminate was vacuum bagged and cured at a maximum temperature of 350°F and pressure of 200 psi. This laminate could not be tested for strength properties due to delamination. This delamination was the result of pressure build-up within the laminate, probably caused by vaporized solvent and/or condensation products.

A laminate was formed at a maximum temperature of 600°F and at a maximum pressure of 500 psi. Part of this laminate showed evidence of delamination; the other part had the highest flexural strength and modulus of any laminate made in the program to date. Laminate PF-21 was formed using CCA-1 carbon cloth as the reinforcement. This laminate was disappointing since the strength values were approximately half of those obtained on carbon cloth-phenolic laminates. The properties of those laminates discussed are summarized in Table I.

Laminates PF-22-1 and PF-22-2 were formed at 1000 psi pressure after being "bumped" five and two times, respectively, at low pressure. Both laminates were pressed at a 300°F maximum temperature with the resultant strength properties relatively high compared to previous laminates formed from J-1 resin. To improve the strength properties of the laminates formed from J-1 resin, another laminate was tried to introduce the layup to a heated press held at temperatures of 806, 850, and 900°F. This attempt at high temperature curing at a pressure of 1000 psi was unsuccessful with resultant poor interlaminar strength. The laminates were of such poor quality that they were not tested.

NASA-Langley PMDA-DAB-DMAc Resin

Two laminates were formed using submitted NASA resin which had been reduced to form a resin with 19.6 percent solids. One laminate was formed at a pressure of 200 psi and the press temperature was raised in 50°F stages from 300 to 600°F over a 3-1/2-hour time period, held at 600°F for 4 hours, and cooled in the press. This laminate did not exhibit any improved strength properties over previous laminates. The PMDA-DAB-DMAc resin used to prepare this laminate gelled when it stood for several days. The gel was mixed with additional DMAc to make up a gel-solvent mixture with the equivalent of 8 percent solids. This mixture was coated on the glass cloth and a laminate prepared from this material following the procedure used for PF-24. The resultant laminate was of such poor quality that all 12 plies could be manually separated. The laminate was not tested for strength properties. The physical properties of these two laminates are recorded in Table II.

Hughes PMDA-DAB-DMAc Resins

Three laminates were formed from Hughes synthesized PMDA-DAB-DMAc resins. The D1516-29X resin was synthesized in technical grade DMAc, the D1516-29Y resin was synthesized in dried reagent grade DMAc and the D1516-29Z resin was synthesized in DMAc at low concentration (2 percent). Examination of the flexural strength data presented in Table II indicates no significant difference between the resins made from technical DMAc or reagent grade DMAc. Laminate PF-28 showed somewhat improved flexural strengths over those strengths obtained from PF-26 and PF-27.

Narmco PMDA-DAB-DMAc Resin

Five laminates were formed using PMDA-DAB-DMAc resin synthesized by Narmco. These five laminates were prepared under identical time, temperature, and pressure conditions but the resin

contents of the individual laminates were varied between 11.1 and 15.5 percent. The laminates formed from Narmco resin showed no improvement in strength properties over those formed using Hughes synthesized resins. The properties of this series of five laminates are tabulated in Table II.

Hughes PMDA-DAB Resins in Various Solvents

Three laminates were formed using Hughes synthesized resins. The D1516-30X resin was synthesized in DMF, the D1516-34R resin in DMAc and the D1516-31X in NMP. All three laminates were formed at 1000 psi pressure and a maximum press temperature of 600°F. Laminates PF-34 and PF-39 exhibited almost identical flexural strength values of the same order of magnitude of previous DMAc resins. Laminate PF-36 experienced delamination during trimming and was not tested. The physical properties of these three laminates are recorded in Table II.

Vacuum Bag Layup

A vacuum bag layup was prepared according to the following procedure. The bagged layup was placed in a press under vacuum with 25 psi pressure for 21 hours with no heat. The temperature then was raised to 300°F over a 20-minute time interval and the pressure increased to 100 psi. The layup was held under these conditions for 1 hour and the temperature then increased to 350°F and held at this temperature for 2-1/2 hours. The bagged laminate was cooled and then placed in a 600°F press for 1 hour at 100 psi and removed hot. The flexural strength and modulus of this laminate were relatively high compared to the laminates previously formed at higher pressures. The physical properties of this laminate are recorded in Table II.

Hughes BTDA-DAB-DMAc Resin

A laminate was formed using a BTDA-DAB-DMAc resin synthesized at Hughes. This new anhydride resin system was investigated to determine if the low strength problems encountered were the result

of the basic resin system as well as solvent-resin interaction. Laminate PF-38 was molded using the same 1000 psi pressure and 600°F maximum press temperature at which the latest PMDA-DAB-DMAc laminates were prepared. Examination of the physical properties recorded in Table II and subsequent comparison to PMDA-DAB-DMAc laminates formed under similar conditions, indicates the BTDA-DAB-DMAc resin system is conducive to the formation of laminates of higher strength than the laminates made from the PMDA-DAB-DMAc resin system.

2.5 MOLDINGS

In order to eliminate the effect of the DMAc solvent it was decided to precipitate the polymer from the DMAc followed by washing and drying operations. The pure polymer then would be used for the molding of pure polymer specimens.

Precipitation of Pyrrone Powders

Initial attempts to precipitate the Pyrrone polymer with water were unsuccessful. The precipitation was done in the 1-gallon blender using 400 ml of H₂O to 100 ml of J-1 resin. After 5 minutes of agitation the slurry was allowed to settle for 1 hour. The pH of the decantant was acidic as measured with litmus paper. The filtered slurry of Pyrrone was dried in a rotary still at 55°C. The polymer fused indicating high residual DMAc.

The Pyrrone polymer was successfully precipitated by blending 100 ml of J-1 resin with 300 ml of acetone in a blender, washing several times, filtering and drying under vacuum. The Pyrrone power produced by acetone extraction is a fine golden yellow powder. Upon exposure to air the surface layer turns light green. The powder is soluble at 10 percent concentration in dimethyl acetamide, dimethyl formamide, N-methyl-2-pyrrolidone and dimethyl sulfoxide. The Pyrrone is essentially insoluble in piperidine.

Molding of Pyrrone Powders

A series of three preliminary Pyrrone moldings was prepared to determine the behavior of the precipitated Pyrrone powder under typical molding conditions. Two 3/4 inch diameter disks were compression molded at 300°F and 3000 psi for 1 hour. These moldings were dense and tough and showed very few voids and flaws. A 2-1/2 inch diameter disk was molded in the same manner as the previous two 3/4 inch disks and then subjected to postcuring from 275° to 600°F over a 66 hour time period. Prior to postcuring the disk had an excellent appearance and a density of 1.26 gm/cc; however, after postcure the specimen showed large blisters and voids indicating volatile emission and low vapor transmission of the material.

Five additional 2-1/2 inch diameter disks were molded from the Pyrrone powder at 300 F and pressures varying between 3000 and 12,000 psi. Not all of these moldings were postcured. The best appearing disks were those molded at the higher pressures with no postcuring. The density of these disks varied between 1.34 and 1.39 gm/cc.

2.6 COATING AND ADHESION STUDIES

Coating and adhesion studies were carried out with unpigmented J-1 resin in DMAc. All studies were conducted using a 20 percent (by weight) solids content resin. Various cleaning and curing procedures were investigated for both stainless steel and aluminum substrates, and the adhesion of the coatings on stainless steel was determined.

Coating of Pyrrone Resin

Forty type 302 stainless steel test coupons (1 x 4 x 0.005 inches) were dip-coated in the 20 percent J-1 resin and air dried at room temperature for periods of 1 to 7 days prior to cure. Surface cleaning and coating cure were the processing variables investigated in this test series. The test coupon surfaces were prepared by both alkaline degreasing methods and depassivation procedures, and both thermal and ionizing radiation techniques were used to cure the Pyrrone

coatings. The most flexible and best adhering coatings were obtained on the electrochemically depassivated substrates which had thermally cured Pyrrone coatings.

Additional coating studies were conducted on both 2024 aluminum alloy and 17-7 PH stainless steel. The aluminum alloy surfaces were prepared by liquid honing, chromic acid immersion and anodic etching in hot alkali. The stainless steel alloy surfaces were prepared by liquid honing, alkaline cleaning and anodic etching in concentrated sulfuric acid. The application of the Pyrrone resin was limited to dip coating with air-drying of each coating prior to recoating. The coatings were cured at either 350° or 400°F in air or by gamma irradiation from a Co⁶⁰ source.

The results of these studies indicated that the surface preparations did not result in the full potential for chemical bond between polymer and substrate to be realized, even where adhesion to the substrates was considered acceptable. These tests further indicated that proper solvent removal and curing may yield acceptable coating film flexibility.

Adhesion of Pyrrone Coatings

Two pairs of test specimens were prepared for 180-degree peel testing. In one case two type 302 stainless steel members, one 1 x 4 x 0.050 inch the other 1 x 4 x 0.005 inch, were detergent cleaned and anodically treated in HCl. Pyrrone resin was brush coated on one side of each member and a layer of glass beads spread on the 0.050 inch thick piece. The two coated surfaces were mated and oven-cured for 2 hours at 400°F. Two such specimens showed no appreciable adhesion or bond line integrity.

A second pair of specimens was prepared from 0.005 inch type 302 stainless steel sheet cleaned in the same manner but dip-coated and air-dried until still tacky. Mating pairs were joined and vacuum dried for approximately 24 hours. One specimen was thermally cured at 400°F for 2 hours and the other cured with gamma radiation in a Co⁶⁰ source. These specimens showed a negligible adhesion of 0.3 pound/inch width at a peel rate of 1 inch per minute.

2.7 DIELECTRIC PROPERTY MEASUREMENTS

A 1/8 inch thick sample of fiberglass reinforced Pyrrone laminate was obtained from NASA-Langley Research Center for X-band dielectric measurements. Three disk specimens of 2.135 inch diameter were evaluated in a resonant cavity dielectrometer at 9.28 GHz at 25°C and one specimen also at 225°C. The results of these tests are presented in Table III.

Specimen	Thickness, inch	Wavelength Per Specimen	Temperature, °C	Relative Permittivity	Loss Tangent
A	0.125	0.1965	25	4.514	0.0463
A + B	0.250	0.3856	25	4.364	0.0365
A + B + C	0.375	0.5757	25	4.328	0.0358
A	0.125	0.1936	225	4.396	0.0098
A	0.125	0.1971	25	4.536	0.0376

Table III. Dielectric Properties of Pyrrone Laminates

The high loss value at room temperature might have been due to absorbed water. After the specimens shown on Table III were dried for 24 hours in a 125°C oven and allowed to cool down in a desiccator, the following were obtained:

A	0.125	0.1890	25	4.213	0.0085
B	0.125	0.1897	25	4.242	0.0083

Thus, it would appear from these preliminary measurements that the subject material is moisture sensitive.

The high temperature (225°C) value reported above is not corrected for the thermal expansion of the specimen. The expansion coefficient of the material is unknown, but if it is assumed a value of 1×10^{-5} per °C the thickness increase for specimen A at 225°C is 0.00025 inch. The "corrected" values of relative permittivity and loss tangent now become 4.38 and 0.0098, respectively.

2.8 DIFFERENTIAL THERMAL ANALYSIS

Differential thermal analyses were run on three powdered Pyrrones obtained by precipitation in acetone. The polymers tested were recovered from J-1 resin (technical DMAc), D1516-29X resin (purified reagent grade DMAc) and D1516-29Y resin (purified technical grade DMAc). All tests were run in a nitrogen atmosphere from ambient to 850°C at a heating rate of 10°C/minute.

All three of the precipitated Pyrrone polymer powder samples behaved similarly. They show initial endothermic character probably due to loss of indeterminate volatiles. In the 120-170°C temperature range the materials begin to exhibit exothermic behavior which continues to the 610-650°C range. This exothermic behavior is relatively broad and not well defined and is most probably due to the curing mechanism. No well defined optimum curing temperature could be determined from the DTA curves. Endothermic decomposition appears to begin in the 600-650°C temperature range.

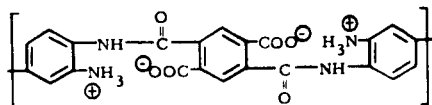
2.9 CONCLUSIONS

The flexural strengths of the Pyrrones prepared in DMAc, DMF, and NMP were lower than anticipated. Three factors probably affected the results. First, the solvent-free or nearly solvent-free resin had very poor flow characteristics. Therefore, it was necessary to leave solvent in the resin in order to provide sufficient flow for processing. Removal of the solvent during the later stages of cure and during postcure consequently left a high void content. Second, the solvent remained tightly bound to the polymer even at high temperatures. Third, at high temperatures the solvent probably reacted chemically with the polymer and possibly interfered with the curing reactions.

The poor flow characteristics were the most important of these factors. In Pyrrones, as in other polymers, weaknesses in the gross structure of the cured polymer exist along boundaries that separate two regions where inadequate flow occurred prior to cure. These

gross structural weaknesses can eclipse completely the strengths or weaknesses inherent in the fundamental chemical structure of the polymer.

The poor flow characteristics of the resin stemmed from the infusibility of the solvent-free polymer. A possible chemical reason for this infusibility lies in the ionic nature of the A-A-A polymer, which can be represented by the zwitterionic structure (XI).



XI

Ionic crosslinking enhances the crystallinity of the polymer and makes it high melting. Conversion of the A-A-A polymer to the polyimide (II) or the polybenzimidazole (III) reduces the ionic character of the polymer, but this offers no improvement in flow properties since the condensed aromatic nuclei formed in the conversion also render the polymer infusible.

A solution to the problem of increasing flow was to reduce the ionic character of the A-A-A polymer. This approach led to the work discussed in Phase II of this program.

The second problem, the tenacity of the solvent, is also the result of the strongly polar nature of the polymer. Because of the polar nature, a strongly polar solvent had to be employed as the synthesis medium. Strong attractions between the polymer and the solvent were inevitable. DMAc, the first choice of solvent, is known to form stable complexes with a variety of organic and inorganic materials with considerable ionic character. For example, DMAc forms a crystalline complex with dicarboxylic acids, the complex containing two moles of DMAc for each mole of acid.¹⁰ It is not surprising, therefore, that this solvent is tenaciously held by the Pyrrone polymers. Eventually, this solvent is removed during postcure and leaves voids that diminish the strength of the cured product.

Fortunately, the solution for the second problem is related to that of the first. Reducing the ionic character of the polymer will permit less polar solvents to be employed. The combination of a less polar polymer and a less polar solvent should minimize the tendency to bind the solvent to the polymer.

The third problem, the stability of the amide solvents at high temperatures, also is peculiar to the amide solvents and could be eliminated with the solvent. The odor of acetic acid detected around the curing polymer was not noticed when purified DMAc was used. Consequently this odor is not necessarily an indication that the solvent had hydrolyzed. However, hydrolysis may still exist as a possible problem, since both the acid and the amine products may remain bound to or reacted with the polymer, as discussed in Section 2. 1. While hydrolysis of DMAc is extremely slow at room temperature, the rate is appreciable at the elevated temperatures required for cure. Further study of these effects was obviated, however, by the approach pursued in Phase II.

During the lamination study it became apparent that flexural strengths on the order of 40,000 psi and moduli of approximately 3 million psi were maximum values for the PMDA-DAB resins in polar solvents. Variation of laminating temperatures and pressures indicated that the best flexural strength values were obtained for intermediate pressure (200 psi to 1000 psi) and temperatures of 600-750°F.

The laminate formed using a BTDA-DAB-DMAc resin exhibited a higher room temperature flexural strength than any of the PMDA-DAB-DMAc laminates prepared in Phase I of the program. This was accomplished with the first laminate tried, with no special techniques employed. The problem of low strengths encountered with the PMDA-DAB laminates was not entirely due to polymer-solvent interaction to form a polyelectrolyte, or to hydrolytic breakdown of solvent during the polycondensation, but was due to the anhydride selected for the polymer system.

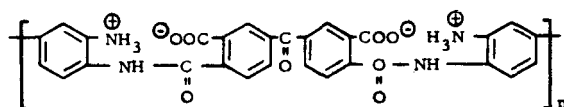
Throughout the laminating program of Phase I an acidic odor of unknown volatile materials emanated from the curing laminates. This odor was not that of the parent solvent, thus it was concluded that the solvent was modified in some manner (probably hydrolysis as a result of reaction with water of condensation) with subsequent oxidation. Attempts to reduce the amount of solvent present in the curing resin met with failure. To maintain the necessary degree of flow to successfully form a laminate, a substantial amount of solvent had to remain in the resin. The resin in its present form had unsatisfactory flow and degradation due to unfavorable behavior of the solvents that appeared to be inherent in the resin system. The Phase II study shows that these assumptions were verified when successful laminates were formed by synthesizing resins that achieved their flow by bonding the solvent internally.

3.0 PHASE II STUDIES

The evaluation of the materials produced in Phase II of the program was based upon the chemical behavior (Sections 3.1 and 3.2), characterization of the resins (Section 3.3), and the physical properties obtained on laminates, special shapes, moldings, foams and precipitated powders (Sections 3.4 through 3.9). The conclusions drawn from this investigation are presented in Section 3.10.

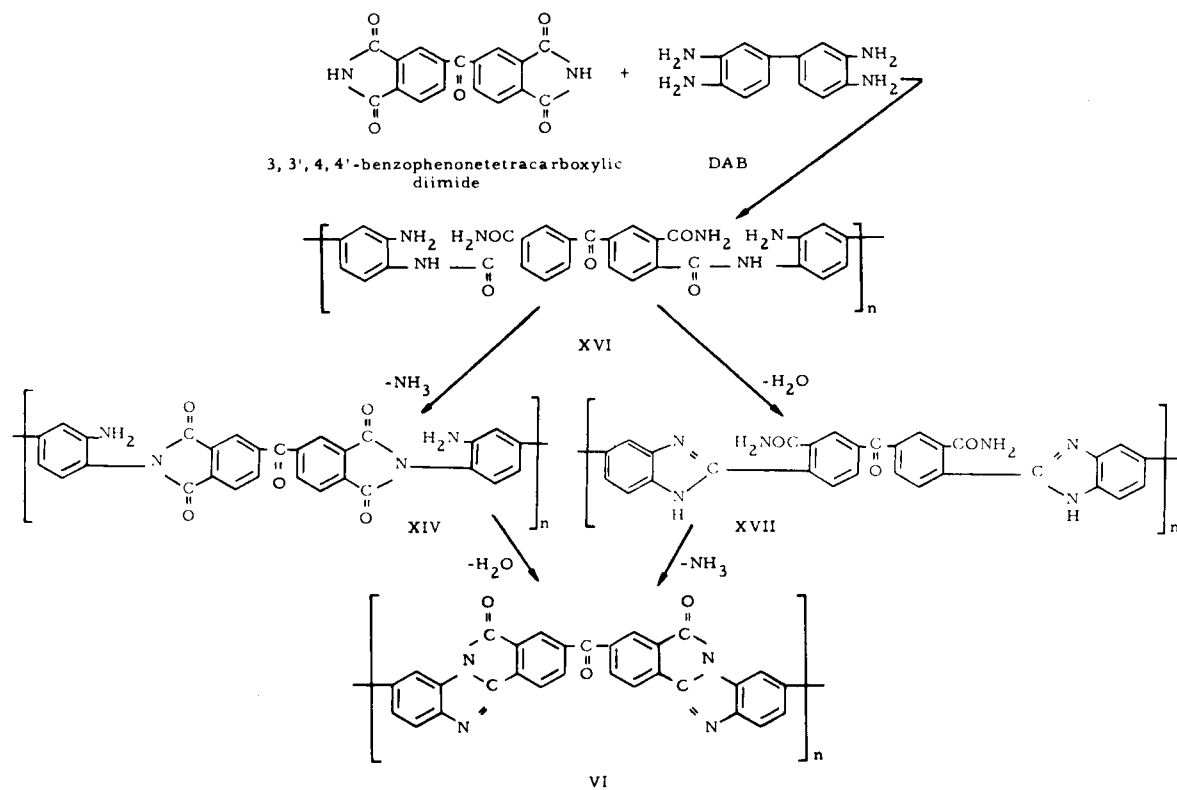
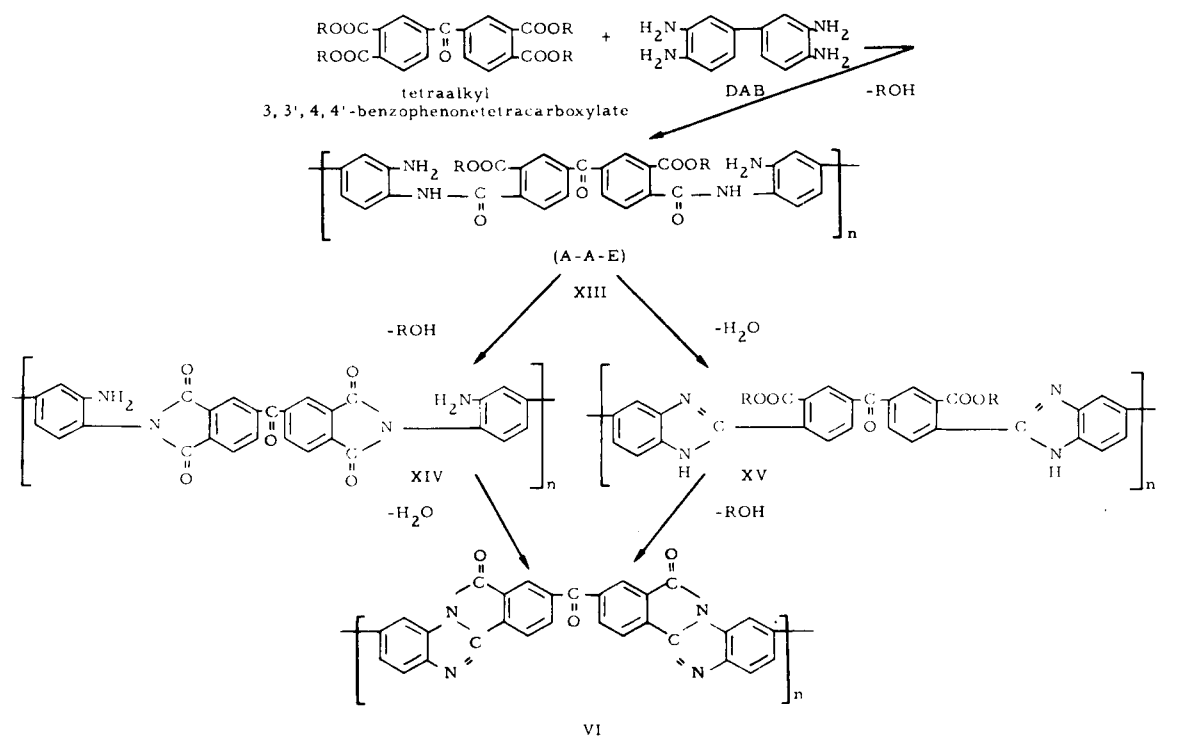
3.1 GENERALIZED REACTIONS

In Phase I of this program it was observed that the solvent-free Pyrrone polymer was infusible and that adequate flow could be obtained during cure only by allowing some solvent to remain in the polymer for the molding process. Infusibility of the polymer, which was actually the amino-acid-amide (A-A-A) polymer, was attributed to the strong electrostatic attractions between the ionic sites on the zwitterionic forms of the A-A-A polymer. For the A-A-A polymer derived from 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 3,3'-diaminobenzidine (DAB) this ionic structure is indicated by (XII).



XII

In order to avoid the formation of an ionic polymer it was decided to employ tetracarboxylic acid derivatives other than the dianhydrides. Esters and imides were suggested as being useful monomers for this purpose, the anticipated reactions are indicated on the following page.



Instead of the A-A-A polymer, the derivatives (XIII and XVI) of the A-A-A polymer are obtained, and the -COOH groups are replaced with the neutral -COOR or -CONH₂ groups. Both processes can produce the same polyimide (XIV) as that obtained by starting with the dianhydride, but different polybenzimidazole derivatives (XV and XVII) are formed. Theoretically, all processes eventually lead to the same Pyrrone (VI). However, none of the intermediates are ionic when the original monomer is either the imide or the tetraester.

The nonionic character of the intermediates was expected not only to improve the flow properties of the polymers during cure but also to enhance their solubility in less polar solvents. Solvents less polar than DMAc should be more easily removed than DMAc, and the problem of hydrolysis of the bound DMAc could be avoided. Of the two possible nonionic intermediates (XIII and XVI), the amino amide ester (A-A-E) polymer (XIII) was preferred since esters generally have lower melting points than amides.

Exploratory work indicated that improved Pyrrones could be obtained by preparing the polymers in ethylene glycol. Therefore, Phase II was undertaken as a study of the use of esters as monomers, with heavy emphasis placed on the esters of ethylene glycol. A concentrated effort was also devoted to the esters derived from BTDA rather than PMDA because of the added flexibility imparted to the polymer by the $\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—} \end{array}$ linkage. Increasing the flexibility of a polymer ordinarily makes it more soluble and fusible.

3.2 SYNTHETIC ROUTES

The first syntheses of BTDA-DAB resins in ethylene glycol (EG) followed the procedure previously employed at NASA-Langley Research Center. A slurry of BTDA in EG was warmed until the BTDA dissolved, and the solution was added to an EG solution of an equal molar quantity of DAB. All operations were performed in apparatus purged with argon, as shown in Figure 3.

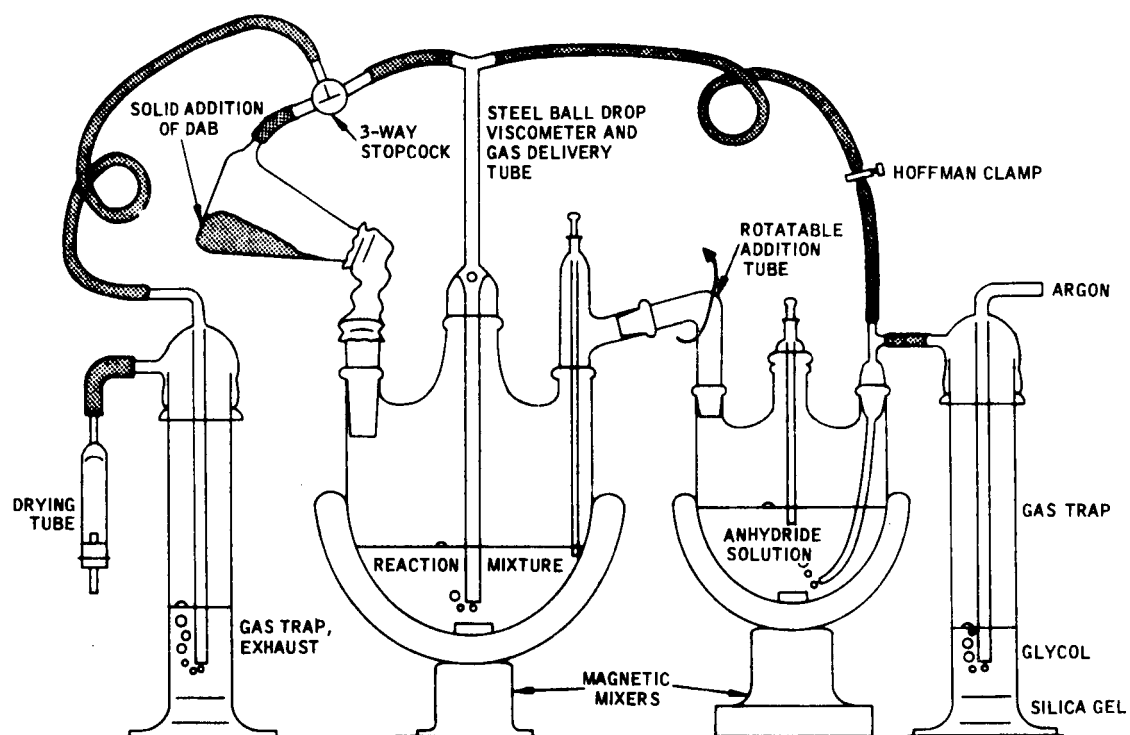


Figure 3. Apparatus for Preparing Pyrrole Resins

Resins Synthesized at Low Solids Content

The reactions were carried out at 75°C, slightly higher than the 60 to 70°C temperatures previously used. Concentrations of reactants used were calculated to give a solution with about 13 percent solids; the resulting solution was concentrated in a rotary evaporator to a solids content of 25 to 30 percent. Experimental details for a specific preparation are as follows.

A 192.6 (0.9 mole) quantity of DAB was added to 1500 ml of purified ethylene glycol at a temperature of 120°C under argon. A solution of BTDA prepared by dissolving 289.6 gm (0.9 mole) of BTDA in 1500 ml of purified EG at 120°C was added to the DAB solution in the reaction vessel, and the mixture was stirred at 70-75°C for 10 minutes. Three batches prepared in this manner were combined and the resultant batch of resin was concentrated to 1 gallon in the Rotafilm evaporator at a temperature of 70-75°C.

A falling ball viscometer was used to follow the progress of such a reaction. Viscosity data were not expected to be precise because the temperature of the reaction mixture could not be precisely controlled. In the first experiments, therefore, the viscometer tube was not jacketed to control the temperature. Because of its high specific heat, however, the EG solution changed temperature very slowly.

Although the DAB solution was already dark in color, the solution turned considerably darker within the first 10 minutes after the BTDA solution was added. An approximately 0.3 molar solution of monomers produced a yellowish flocculent precipitate after 410 minutes at about 75°C. During this time the viscosity of the solution increased from 25 to 81 centipoises. No sudden changes in viscosity or appearance occurred. Prolonged heating merely caused the precipitation of additional material. The polymer so derived was a "brick dust" type of material that was insoluble in all solvents tested but concentrated sulfuric acid. Although it failed to melt on a melting point block, it underwent sufficient flow in a press to allow a part to be molded.

When a similar reaction was carried out at 100°C, polymer precipitated only 28 minutes after mixing. No appreciable increase in viscosity could be detected prior to precipitation, however. Lower temperatures were definitely more desirable for controlling the extent of reaction.

Resins Synthesized at Higher Solids Content

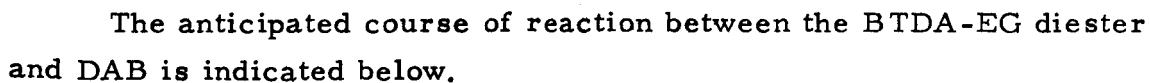
Evaporation of solvent in the rotary evaporator not only was a time-consuming process, but it also advanced the resin to an undetermined extent. Bath temperatures of 70 to 75°C were required, although the temperature of the evaporating solution actually may have been considerably lower. It was found that more concentrated resins could be prepared directly from more concentrated solutions of the monomers. Most of the subsequent solutions were prepared in such a manner that the weight of BTDA and DAB used equaled about 23 percent of the weight of the final solution. This concentration, that will hereafter be called a 23 percent solids concentration, was found to be quite satisfactory for coating the reinforcing fabric. Experimental detail for a typical preparation of this type follow.

A solution of BTDA composed of 193.2 gm (0.6 mole) in 300 ml of EG at 76°C was mixed with a DAB solution composed of 128.4 gm (0.6 mole) in 735 ml of EG at 75°C. The temperature rose to 78°C on mixing, and after about 10 minutes the resultant resin was cooled and stored under argon.

A temperature of 75°C or greater was necessary to retain the DAB in solution at the concentration required for preparation of a 23 percent solids resin. At this temperature and concentration the polymer began to precipitate after about 320 minutes. At this point the polymer was more soluble in the reaction mixture than it was in EG; consequently, the polymer that precipitated from the concentrated solution may have been more advanced than that first precipitated from a more dilute solution.

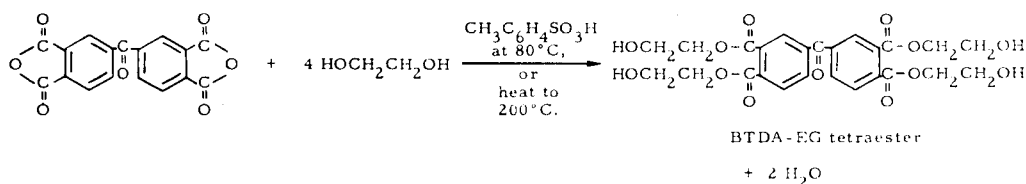
The viscosities of the more concentrated reaction mixtures were determined with a falling ball viscometer that had been jacketed and surrounded with the bath fluid to maintain better control of the temperature. As the reaction progressed the viscosity at 75°C increased from an initial value of 26 centipoises to about 50 centipoises at the point of precipitation.

In carrying out these syntheses it was observed that BTDA was not soluble in EG at room temperature, but that once the mixture was heated to dissolve the BTDA nothing precipitated on cooling to room temperature. Obviously the dissolution process involved an esterification reaction like that shown by the equation below.



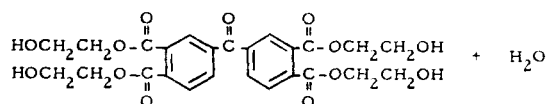
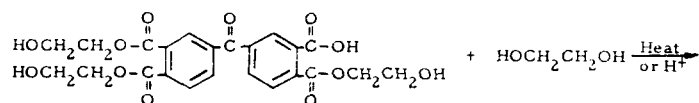
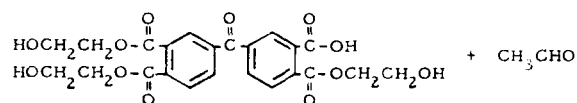
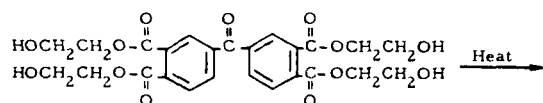
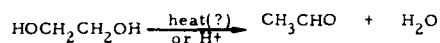
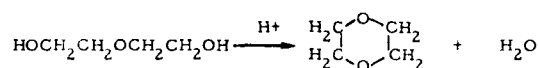
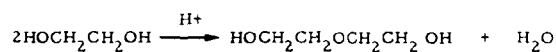
Thus the initial product of the reaction would be a salt of the monomers. Condensation to form a polymer from the salt would be anticipated to lead to the A-A-A polymer (XVIII) or its zwitterionic form (XII). The alternative reaction, in which water would be eliminated and the polymeric product would retain the ester groups, is considered much less probable since aminolyses of esters ordinarily occur far more readily than aminolyses of carboxylic acids. If the A-A-A polymer was indeed the product, the basic structure of the polymer was unchanged from that secured from the anhydride and DAB in DMAc. The differences in behavior probably were due to differences in molecular weight and in end groups. Since the anhydrides are extremely reactive toward amines, the polymerization probably continued unabated until a high molecular weight polymer was formed. The esters, on the other hand, were less reactive, and polymerization could be arrested, or spontaneously arrested by precipitation from EG, when the polymer had a relatively low molecular weight.

In view of the probable course of reaction, it was considered desirable to convert BTDA (or the BTDA-EG diester) to the tetraester prior to reaction with DAB. This conversion was carried out both with and without an acid catalyst.



The acid-catalyzed esterifications were conducted at the boiling point of a glycol-benzene mixture in the presence of p-toluenesulfonic acid as a catalyst. Water was removed as the benzene azeotrope. The uncatalyzed esterifications were accomplished at the boiling point of the glycol solution, with the water being removed continuously by distillation. Both methods produced considerably more than the theoretical amount of water and the quantity of water produced, therefore, served

only as a vague indication of the completeness of reaction. Possible sources of water other than the esterification are indicated by the following equations:



Water-producing side reactions interfered most in the acid-catalyzed reaction; consequently, the uncatalyzed reaction seemed preferable. Since the product of the acid-catalyzed reaction was noticeably more viscous, the telomerization of glycol is assumed to be the primary side reaction. Water derived from the uncatalyzed esterification had the distinctive odor of acetaldehyde; however, a semi-carbazone prepared from the aqueous distillate was not the acetaldehyde derivative. The ester was used in the solution in which it was prepared without purification. Several typical ester preparations are described as follows.

A 96.6 gm (0.3 mole) quantity of DAB and 1.0 gm of p-toluenesulfonic acid monohydrate were dissolved in 150 ml of hot EG. The solution was cooled to below 80°C, 200 ml of benzene was added and the mixture was refluxed for 48 hours under an azeotropic trap. From this reaction, 17 ml of lower phase was collected in the distillate, and a refractive index indicated it was practically 100 percent water. (Theoretical water of reaction was 10.8 ml.) The benzene was distilled from the mixture to leave the ester solution, which was an extremely viscous liquid with very little tendency to flow.

Another ester was prepared by adding 96.6 gm (0.3 mole) of BTDA to 530 ml (585.1 gm) of purified EG which had been heated to 110-130°C. The reaction mixture began boiling at 180°C with further heating. As the water which formed was distilled from the mixture, the temperature of the boiling mixture rose to 199°C. During the distillation the temperature at the top of the distillation column never rose above 178°C. The total aqueous distillate weighed 28.17 grams, had a light yellow color, possessed an odor reminiscent of acetaldehyde and had a refractive index (sodium D at 25°C) of 1.3547 which corresponds to a composition of 22 volume percent glycol - 78 volume percent water. An additional 24.4 grams of solvent with a refractive index of 1.4284 (corresponding to a 97 percent glycol - 3 percent water composition) were distilled off leaving an ester solution weighing 627.6 grams. A Karl Fischer titration of the two fractions of distillate indicated they contained 85.1 percent and 3.9 percent water. Thus the Karl Fischer method showed that the total yield of water was 24.9 gm, whereas the estimate based on the refractive indices was 22.7 gm. Theoretically the yield should have been 10.8 gm for the esterification.

Since the ester has not yet been characterized (although it has been determined that it can be isolated as a solid), and since side reactions are clearly occurring during the esterification, it still is not known that the product is actually tetrakis(2-hydroxyethyl) 3,3',4,4'-benzophenonetetracarboxylate. It seems safe to assume, however, that it is a more completely esterified product than that obtained by simply dissolving the dianhydride in EG. Whatever the actual structure is, it will be referred to as the BTDA-EG tetraester.

The BTDA-EG tetraester probably contains a small amount of low molecular weight polyester, although polyester formation was suppressed by using a huge excess of ethylene glycol. When the preferred procedure was used, even at the end of the esterification the molar ratio of glycol to ester was 26:1 and the ratio of equivalents of hydroxyl groups on the ester to equivalents of hydroxyl groups on the glycol was 13:1. BTDA-EG polyester should be cleaned by DAB to give the same products as those formed from the simple tetraester.

The first preparation of the tetraester is believed to have been incomplete. A reaction of this product with DAB for 5 hours at 75°C produced a polymer which was insoluble in the cold resin but soluble in the warm resin at a concentration of about 30 percent solids. Condensation of a more completely esterified product with DAB gave no precipitate after 4 days at 100°C. In both cases there was little change in viscosity during the reaction, but the solution became darker in color. A 5 percent excess of BTDA-EG tetraester did not change this behavior. Obviously the use of the BTDA-EG tetraester instead of the diester caused a considerable change in the nature of the reaction products.

Heating the reaction mixture containing DAB and the BTDA-EG tetraester at reflux for about 1-1/2 to 3 hours (depending on the prior treatment) formed a resin that became extremely viscous on cooling or even gelled at the reaction temperature. The formation of a thick, gummy paste or gel-like product, rather than a granular precipitate such as that obtained from DAB and the BTDA-EG diester, was a noteworthy feature of these preparations. This behavior was consistent with diminished ionic character and a lower degree of crystallinity.

The progress of the polymerization was followed by making relative measurements of the viscosity of the solution. The column of liquid in the falling ball viscometer was not maintained at a constant temperature; but by making measurements in the same manner each time, adequate relative values could be obtained in spite of gradual cooling of the solution. The viscosity increased from less than 10 centipoises to about 30 centipoises at the time of gelation.

Resins Synthesized from BTDA-EG Esters

A series of resins was prepared from DAB and BTDA-EG tetraester. The solid DAB was dissolved in the EG solution of the tetraester at about 100°C, and the resulting solution was then heated to reflux as illustrated by the following typical resin preparation.

A 615.8 gm quantity of 0.3 mole BTDA-EG tetraester solution was heated to 100°C under argon and 64.2 gm (0.3 mole) solid DAB was added. The mixture was stirred and heated to reflux. Periodic viscosity readings were taken at the reflux temperature. After 2 hours the viscosity had increased from 5.0 to 13.5 centipoises. The mixture was cooled rapidly in an ice bath and the resultant resin was stored under argon. The cooled resin was an extremely viscous, non-pourable resin.

A plot of viscosity against reflux time indicated that the results were not readily reproducible, probably because of variations in the time required to reach the reflux temperature. Viscosity readings appeared to be a more reliable method than reflux time for monitoring the extent of resin advancement. From this study it was concluded that at a 23 percent solids concentration, the viscosity of the refluxing reaction mixture should not greatly exceed 7.6 centipoises if a resin of workable fluidity at room temperature is desired.

A better correlation between reaction time and viscosity could be obtained by adding the solid DAB to the refluxing BTDA-EG tetraester solution. An unexpected result, however, was that the viscosity increased much more rapidly than it did when the initial addition of DAB was made at 100°C, and the solution was subsequently heated to reflux temperature. For example, when the initial addition of DAB was made at 100°C and the reaction mixture was subsequently heated at reflux for 2 hours, the viscosity was the same as that of a similar reaction mixture obtained by adding the DAB to the ester at the reflux temperature and heating the mixture at reflux for only 30 minutes. Furthermore, the products of the latter type of preparation were more fluid at room temperature. Possibly the reactions initiated at the boiling point are different from those which occur when the reactions are initiated at

lower temperatures. This could be a consequence of competitive reactions with different activation energies.

The viscosities of the reaction mixtures increased gradually and smoothly at the reflux temperatures. When the mixtures were cooled to room temperature those mixtures that had a viscosity of less than 10 centipoises, at the reflux temperature, remained fluid. However, those mixtures that had a viscosity greater than 10 centipoises, at the reflux temperature, became extremely viscous.

This behavior is best illustrated by a series of four resins prepared in the following manner. All four resins were prepared by adding 64.2 gm (0.3 mole) of solid DAB to 610.8 gm (0.3 mole) portions of the ester solution while the ester was being stirred at gentle reflux under argon. Viscosity measurements were made periodically at the reflux temperature. After the reactions had proceeded to the desired degree of advancement, as determined by the viscosities, the mixtures were cooled in ice and stored under argon. The viscosities at the reflux temperature and the appearance of each at room temperature are presented in Table IV.

Run D1516-59		Run D1516-60		Run D1516-62		Run D1516-61	
Viscosity, centipoises	Reaction Time, minutes	Viscosity, centipoises	Reaction Time, minutes	Viscosity, centipoises	Reaction Time, minutes	Viscosity, centipoises	Reaction Time, minutes
6.5	8	6.5	8	5.5	7	5.5	8
7.5	20	7.0	16	7.0	24	8.0	34
7.5	25	7.5	25	8.0	44	9.0	44
		8.5	35	10.0	69	10.0	59
		9.5	43	11.0	89	11.0	74
						12.0	84
						13.5	94
Easily pourable		Slightly less pourable than D1516-59		Barely pourable		Still pourable but even less so than D1516-62	

Table IV. Viscosity Properties of a Series of BTDA-DAB-EG Resins

Resins were also prepared from PMDA and DAB using essentially the same procedures that were developed for the BTDA-DAB resins; however the PMDA-EG esters were used in these preparations.

Resins Prepared from BTDA-ETOH Esters

Since EG has a very low volatility and is lost only very slowly during laminating, it was thought advisable to compare the BTDA-DAB resins prepared in EG with similar resins prepared in a more volatile alcohol. Therefore, resin was synthesized from DAB and an ester that presumably was tetraethyl 3, 3', 4, 4'-benzophenonetetracarboxylate, the BTDA-ethanol tetraester. Since, however, polymers are quite insoluble in ethanol, the polymer had to be synthesized in what was essentially a melt of the monomers with some residual ethanol.

The BTDA-ethanol ester was prepared by adding 96.6 grams (0.3 mole) of BTDA to 500 ml of hot absolute ethanol with subsequent dropwise addition of 20 ml of concentrated sulfuric acid. Upon addition of the acid, the BTDA went into solution and the reaction mixture was stirred at reflux for 20 hours. The ethanol was then distilled from the reaction vessel until the temperature above the reaction mixture rose above 100°C. The volume of the reaction mixture at this point was approximately one-third of the original volume. The resultant crude mixture was taken up in ether, washed several times with water, and then shaken with 10 percent sodium bicarbonate solution until acidification of the bicarbonate washes failed to produce a precipitate. The ethereal solution was then dried over anhydrous magnesium sulfate. Finally, the ether was evaporated and a product weighing 89.3 gm was collected (63 percent of theoretical).

The BTDA-DAB-ETOH resin was prepared by mixing 89.3 gm (0.19 mole) of the prepared ester with 500 ml of absolute ethanol, heating to reflux under argon and adding 40.5 gm (0.19 mole) of solid DAB. This mixing produced a slurry which was stirred vigorously. Excess ethanol was distilled out of the reaction mixture and the temperature was allowed to rise to 150°C, at which point the mixture became a viscous melt. The temperature kept at 150°C for 15 minutes, then raised to approximately 200°C. After 90 minutes at these conditions,

the mixture became too viscous to be stirred, and the reaction was discontinued. On cooling, the melt became a brittle glass weighing 108.4 gm. DAMc and DMF are solvents for the resin and can be used to prepare a solution. These solvents may be more satisfactory with the esterified polymer than they were with the A-A-A polymers prepared in the amide solvents.

3.3 CHARACTERIZATION OF RESINS

During Phase II it became apparent that the approach taken in synthesizing the resins in ethylene glycol resulted in properties that enabled laminates of greater strength to be formed. The criterion selected for evaluation of the resins was again the flexural strength and modulus that could be attained with the particular resin under evaluation. During the synthetic and processing phases, a better understanding was achieved of the performance of the ethylene glycol systems. Resins more conducive to the laminating operation were designed and higher strength laminates achieved. At this point in the program a significant amount of the effort was directed toward synthesis and processing studies with a minimum degree of effort toward detailed resin characterization. Only information was sought that was necessary to direct changes in synthetic routes that would result in resins conducive to laminating operations and improved strength laminates. It was believed that once a workable standard resin was selected, more effort could be directed to a detailed investigation of this system.

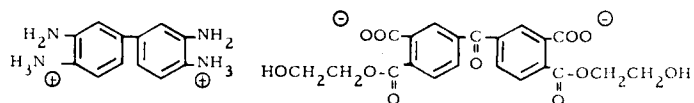
The following sections detail the cursory investigations conducted during the synthesis-fabrication aspects of the program to give a better "feeling" for the BTDA-DAB-EG systems.

Molecular Characterization

The molecular structures of the polymers prepared in EG have been characterized very briefly. At this time, only solubility data and elemental analyses - in addition to the methods of synthesis are available for making inferences about structural characteristics.

In general, solvents such as chloroform, trichlorobenzene, acetone, dioxane and methanol are very poor solvents for these polymers, while the more polar solvents such as DMSO, DMAc and DMF are more effective. EG lies between these two groups in its ability to dissolve the polymeric products.

When the BTDA-EG diester is reacted with DAB, the first product formed is a salt of the tetraamine and the dicarboxylic acid:



When the reaction time was kept to a minimum at a temperature of 75°C, possibly the reaction did not proceed far beyond the point of salt formation. The precipitates formed after several hours of reaction, however, were obviously polymers and not merely a salt of the two reactants. The product that first precipitated was readily soluble in dilute aqueous base, indicating that the product at this point had free carboxyl groups. Also, it was soluble in solvents more polar than EG, solvents such as DMAc and DMSO. A similar precipitate heated for a longer time at temperatures up to 100°C was insoluble in all solvents tested except concentrated sulfuric acid. This decreased solubility probably was due to conversion of the polymer to a polyimide structure, in which the free carboxyl groups are no longer present.

A polymer that precipitated from a reaction mixture of DAB and BTDA-EG tetraester was insoluble in cold dilute aqueous base but dissolved quickly upon heating. Probably the dissolution was accompanied by the hydrolysis of the ester groups, since the material remained in solution after cooling. The solubility characteristics gave no indication that cyclization occurred to any significant extent.

An indication of the complexity of the polymerization reaction in EG was obtained from the elemental analyses of precipitated polymers. The results are presented in Table V. Resins D1516-37 and D1516-43 were made from what was assumed to be BTDA-EG diester diacid, while D1516-48 was made from the more fully esterified BTDA-EG system (tetraester). All of the products precipitated or gelled in the reaction mixture and were washed repeatedly in methanol and dried thoroughly under vacuum. (It was noted that the washings from D1516-43 turned dark on standing, apparently due to air oxidation of amino compounds.)

	Resin System		
	D1516-37	D1516-43	D1516-48
Percent carbon	63.17	62.22	60.62
Percent hydrogen	4.56	4.83	5.73
Percent nitrogen	8.29	7.64	5.88
Percent oxygen (by difference)	23.98	25.31	27.77
Moles DAB/mole BTDA	0.92	0.89	0.86
Moles EG/mole BTDA	2.31	3.08	7.06
Moles H ₂ O removed/ mole BTDA	2.32	2.82	6.85

Table V. Elemental Analysis and Mole Ratios of Precipitated Polymer Powders

The analyses indicated the polymers were all lower than theoretical in nitrogen and higher than theoretical in hydrogen. A more detailed analysis of the results was made by setting up four equations for each polymer (P) as follows. (The percentage of oxygen in these analyses was obtained by difference.)

$$\frac{\% \text{ C in BTDA}}{100} x + \frac{\% \text{ C in DAB}}{100} y + \frac{\% \text{ C in EG}}{100} g = \frac{\% \text{ C in P}}{100}$$

$$\frac{\% \text{ N in DAB}}{100} y = \frac{\% \text{ N in P}}{100}$$

$$\frac{\% \text{ H in BTDA}}{100} x + \frac{\% \text{ H in DAB}}{100} y + \frac{\% \text{ H in EG}}{100} g + \frac{\% \text{ H in HOH}}{100} w = \frac{\% \text{ H in P}}{100}$$

$$\frac{\% \text{ O in BTDA}}{100} x + \frac{\% \text{ O in EG}}{100} g + \frac{\% \text{ O in HOH}}{100} w = \frac{\% \text{ O in P}}{100}$$

These equations then were solved simultaneously to obtain x, y, g, and w (the weight fraction of each in the polymer). This analysis assumes that all possible polymer structures are derived from some chemical or physical combination of BTDA, DAB, and EG accompanied by the elimination of water in certain reactions. As anticipated, the weight fraction of water (w) was a negative quantity in each case.

The results of these analyses are expressed in Table V as the moles of each component per mole of BTDA. The reliability of these values has not yet been established, but certain general conclusions appear to be justified. First, there is an unexpectedly large amount of EG or EG derivative in each polymer, with the amount being highest in that derived from the tetraester. The amount present in the polymer, however, far exceeds the amount (4 moles) theoretically present in the tetraester itself. Second, the BTDA moieties exceed the DAB moieties in all cases. The BTDA/DAB ratio is 1.12 (± 3 percent) for all three polymers. The ratio of reactants could have been modified, however, by washing out the more soluble components, if these were rich in amine content. Third, the number of moles of water lost is very nearly the same as the number of moles of EG moieties present — the ratio of EG to H_2O being 1.04 (± 5 percent) for all cases. This similarity would be anticipated if the glycol is all present in the ester form (except for those ester groups formed by reaction with the anhydride), but it is also true when the amount of glycol exceeds by far the amount theoretically allowed. Moreover, the water loss calculated for the tetraester polymer exceeds that assumed for a fully cured Pyrrone

(4 moles/mole of BTDA). Obviously, it would be desirable to know more about the nature of the EG-derived groups present in the polymer.

More data is required to determine the utility of this method for the polymer characterization. It could be very useful method, since it is applicable to both soluble intermediates and insoluble or cured products.

Viscosity Measurements

The BTDA-DAB polymer synthesized in ethylene glycol and concentrated to 30 percent solids was subjected to viscosity measurements on an Ostwald-Fenske viscometer at 25°C.

It became apparent at a concentration of 0.157 gm/dl that the viscosity study would have to be curtailed since the average efflux time was less than that of the pure solvent. At this time, the only explanation for this phenomenon is that the hygroscopic nature of the ethylene glycol caused a dilution of the resin by water absorption.

Another interesting phenomenon was that of a curdling which occurred when the 30 percent resin was diluted to a concentration of 3.56 gm/100 ml. The dilution was accomplished by adding 10 ml of the 30 percent resin to a 100 ml volumetric flask and adding pure ethylene glycol to the reference mark. Upon shaking the flask lighter colored curds of material appeared in the dark solution. Throughout the viscosity run the diluted resin had the appearance of a suspension rather than a true solution (i. e. , turbid rather than clear) indicating that the curds did not re-dissolve but were stable in dilute solution. The dilute solution was heated also to 50°C with shaking and did not appear to clear up. The reason for this behavior was not determined and the viscosity study was curtailed at this point. It was felt that the viscosity determinations again could be resumed when resins which are more conducive to high strength laminate formation are produced.

Dynamic Modulus

An attempt was made to determine the viscoelastic behavior of the same resin, using the vibrating reed technique.

Three dip coats were coated on substrates of stainless steel, beryllium-copper and a three-ply glass cloth-Pyrrone laminate with drying at 130°F between coatings. No distinctive change in dynamic modulus was observed when the reeds were heated from ambient to 580°F. Examination of the reeds after heating to 580°F showed a tough dark colored skin on the surface of the hardened Pyrrone and a yellow foam-like underlying layer. It appears that the resin at the surface can readily lose the ethylene glycol to form a very hard dense skin which in turn prevents the loss of the glycol from the resin beneath the resultant skin. This foam-like material has very poor adhesion to the reed substrate material with the net result that any change in dynamic modulus that occurs cannot be detected because the fundamental frequency of the system is not shifted to any appreciable degree.

Another effort was attempted to detect a change in dynamic modulus by loading the surface of the glass cloth 3-ply laminate with the fluid resin and heating this system. The glass cloth laminate substrate appears to be the most sensitive to changes in modulus but the adhesion problem will have to be solved before reliable data with no discontinuities can be developed.

Cure Plate Gel Times

The "gel" times of both a 30 percent solids BTDA-DAB-EG resin and a 20 percent solids PMDA-DAB-EG resin were determined using the cure plate method. In this method, several drops of the resin were dropped onto a hot plate at the temperature of interest and were repeatedly squeezed between the hot plate and a spatula until threads of polymer began to form. The threads were stretched repeatedly until the material became too viscous to form anymore threads. The time from when the resin first touched the hot plate until the material no longer formed threads was recorded as the "gel" time.

These times gave a good indication of the time period during which the respective resins possessed reasonable flow characteristics and thus were conducive to optimum laminate formation. The BTDA-DAB-EG resin tested had "gel" times which varied from 172 seconds at 250°F to 24 seconds at 350°F while the PMDA-DAB-EG resin had times which varied from 280 seconds at 250°F to 43 seconds at 350°F.

The "gel" time also served as a method for checking the stability of the resins. Since BTDA-DAB-EG D1516-53 appeared to be one of the better resins and was used to form several laminates, it was selected for a stability study. The "gel" time of this resin was determined at 450, 475, and 496°F and a portion of the resin was allowed to stand at room temperature for 11 days in a closed container. This resin had "gel" times of 100 seconds, 69 seconds and 46 seconds originally for the respective 450, 475 and 496°F temperatures. A recheck of the D1516-53 resin after 11 days showed no change of "gel" times thus indicating no significant advancement of the resin at room temperature.

3.4 LAMINATING AND PHYSICAL PROPERTIES

A series of glass cloth laminates was molded from various types of BTDA-DAB resins that had been synthesized in ethylene glycol. The initial BTDA-DAB-EG resins were synthesized under rather mild reaction conditions and were considered to be of the diacid-diester type. The latter laminates were molded from the more fully esterified resins that were designated as the tetraester type. The knowledge gained from the Phase I laminating program along with DTA analysis of the ester type material was put to good use; the net result was the formation of a greater number of successful laminates. The same criteria were used to judge the usefulness of the particular resin system under evaluation. These criteria were flexural strength and modulus, retention of room temperature strength at elevated temperatures, and volume percent voids in the resin matrix. A description of the particular behavior of the resins used for laminating purposes is detailed in the

following sections. All laminates were molded using style 181 glass cloth with an A1100 finish.

NASA-Langley BTDA-DAB-EG Resin

During Phase I of the program it was shown that the laminate that exhibited the greatest flexural strength was molded with a BTDA-DAB type resin. This observation along with the suspected degradation of the laminates as a result of detrimental polymer-solvent interaction led to evaluation of BTDA-DAB type resins synthesized in ethylene glycol. The results of an investigation of this type resin synthesized at 33 percent solids by NASA - Langley are given in Table VI.

Two laminates were formed from the BTDA-DAB-EG submitted by NASA - Langley under conditions similar to the formation of Phase I laminates. Although no drastic changes occurred in the laminating conditions, there was an immediate improvement of flexural strengths and moduli. Flexural strengths on the order of 60,000 psi and moduli as high as 5×10^6 psi were achieved with the NASA resin. Since this BTDA-DAB-EG resin demonstrated a marked improvement in the physical properties of laminates formed from it, synthesis of this type resin was initiated at Hughes. Several resins of the BTDA-DAB-EG type designated D1516-35 and D1516-36 were synthesized. Laminates formed from these resins are described in the following section.

Hughes Diacid-Diester BTDA-DAB-EG Resins

A laminate was formed using prepreg which had been dried at 180°F for 45 minutes in a forced draft oven. The physical properties of this laminate are recorded in Table VI along with the conditions under which it was formed. The strength of this laminate was rather disappointing, thus the drying conditions of the prepreg were changed from 180°F drying in a forced draft oven to 170°F drying in a vacuum oven and 1500 psi pressure in the press. This treatment of the material resulted in much improved strength properties. Drying conditions of 180 and 160°F in a vacuum oven were tried for several laminates. Drying at 180°F in a vacuum oven resulted in better strength properties

than the 160°F drying. The pressure also was dropped to 1250 psi to reduce resin "squeeze out." This pressure was used throughout the remainder of Phase II laminating studies to reduce the variation due to changing laminating pressures.

Hughes PMDA-DAB-EG Resin

A PMDA-DAB-EG resin was synthesized following the same procedure used to produce the BTDA-DAB-EG resins. A laminate was formed from a resin of approximately 20 percent concentration under conditions of pressure and temperature identical to those used to form the BTDA-DAB-EG laminates. The results of this investigation indicate an appreciable increase in strength over the PMDA-DAB-DMAc systems investigated in the Phase I laminating studies. This verifies the prediction that the improved flow characteristics to be expected from resins synthesized in esterifying solvents would result in improved strength. Examination of the physical properties of PF-45 recorded in Table VI indicate that these improved strength characteristics were achieved.

Staged Heating in Press

Several laminates were formed under similar conditions of pressure and temperature with the press temperature increased step-wise during the molding operation. One prepreg was dried 2 hours at 180°F in a vacuum oven while the other prepreg was dried for 1-1/2 hours at 180°F in the vacuum oven. The resultant differences in strength properties due to this variation in the drying treatment are recorded in Table VI. The shorter drying period used for PF-47 prepreg resulted in a much higher strength in the laminate. This indicates that the ultimate strengths to be developed in laminates formed from this type resin system are very sensitive to the treatment given the prepreg material.

Combined Effects of Press Temperature and Postcure

At this point in the investigation since a systematic study of the effects of press temperature and postcuring in both air and argon appeared to be warranted an experiment was set up.

Each prepreg was prepared by applying three spatula coats of 30 percent BTDA-DAB-EG resin to style 181 glass cloth with an A1100 finish. Each successive coating was dried for 15 minutes at 180°F and the prepreg was cut into 6 x 8 inch plies. These plies were held at 180°F in a 28, 5-inch vacuum for 105 minutes. The vacuum oven-dried plies were used to form four 6 x 8 inch - 12-ply laminates. These four laminates were introduced into a press at 275°F and 1250 psi pressure was applied. The press temperatures were varied from 275° to 500°F at 75°F increments to give four temperature conditions.

Upon completion of the pressing stage the finished laminates were cut into two equal halves and the halves postcured in either air or argon by a programmed heating cycle which increased the temperature from 275 to 600°F over a 48-hour period. The laminates were held at 600°F for 2 hours, allowed to cool to below 200°F and removed for further testing.

After completion of the postcuring, the finished laminates were cut into specimens for flexural strength and modulus determinations. The results of these tests are recorded in Table VI for laminates PF-48A and PF-48AR through PF-51A and PF-51AR. Close examination of the physical properties for this series of eight laminates indicates that the best strength properties are achieved by a maximum press temperature of 350°F, and in all cases the argon postcure gives higher strength laminates than the air postcure. The physical properties of the BTDA-DAB-EG laminates postcured in air and argon are recorded in Table VI.

Resins of Higher Concentration

In an effort to determine the effect of resins synthesized at higher concentrations rather than concentrated by distilling off solvent, laminates were formed from two Hughes synthesized resins. A series

Laminate Designation (1)	Resin Designation (2)	Laminating Conditions			Final Resin Content percent	Density, gm/cc	Volume Percent Voids in Resin, percent	Average Flexural Strength (psi x 10 ⁻³)		Average Modulus (psi x 10 ⁻⁶)		Remarks
		Contact Time, minutes	Maximum Pressure, psi	Temp. Range, °F				Room Temp.	Elevated Temp.	Room Temp.	Elevated Temp.	
PF-35	NASA-Langley	3 ⁽⁴⁾	200	275-600	25.5	1.52	46.7	68.1	42.4 ⁽⁸⁾ 39.0 ⁽⁹⁾	3.25	2.42 ⁽⁸⁾ 2.35 ⁽⁹⁾	Laminate non-uniform in appearance
PF-37	NASA-Langley	3 ⁽⁴⁾	1500	275-600	12.4	1.91	47.8	59.9	49.6 ⁽⁸⁾ 52.2 ⁽⁹⁾	5.12	4.76 ⁽⁸⁾ 5.18 ⁽⁹⁾	Varnish wet cloth thoroughly
PF-41	D1516-35	0 ⁽⁴⁾	1000	275-600	24.9	1.61	41.8	33.9	35.6 ⁽¹⁰⁾ 6.9 ⁽¹⁰⁾	2.69	2.96 ⁽¹⁰⁾ 1.72 ⁽¹⁰⁾	Edges porous and surface mottled
PF-42	D1516-35	0 ⁽⁵⁾	1500	275-600	27.8	1.73	28.0	62.8	43.1 ⁽¹⁰⁾ 12.3 ⁽¹⁰⁾	3.90	3.12 ⁽¹⁰⁾ 2.46	Laminate had a uniform appearance
PF-43	D1516-36	0 ⁽⁵⁾	1250	250-600	31.3	1.71	24.2	63.8	33.5 ⁽¹⁰⁾ 37.6 ⁽¹⁰⁾	3.78	2.65 ⁽¹⁰⁾ 2.89 ⁽¹⁰⁾	Laminate was solid and appeared uniform
PF-44	D1516-36	0 ⁽⁵⁾	1250	250-600	17.3	1.84	40.0	44.9	34.0 ⁽¹⁰⁾ 14.1	2.34	2.09 ⁽¹⁰⁾ 1.97 ⁽¹⁰⁾	Laminate showed good resin squeeze out
PF-45	D1516-36 ⁽³⁾	2-1/2 ⁽⁵⁾	1250	275-600	19.3	1.83	36.1	57.2	43.1 ⁽¹⁰⁾ 9.3 ⁽¹⁰⁾	4.39	4.06 ⁽¹⁰⁾ 3.10 ⁽¹⁰⁾	Laminate felt solid and had good edges
PF-46	D1516-36	0 ⁽⁵⁾	1250	275-600	32.9	1.70	26.6	56.4	38.0 ⁽⁸⁾ 38.3	*	*	Indication of slight edge delamination
PF-47	D1516-36	1-1/2 ⁽⁵⁾	1250	275-600	22.4	1.77	38.2	75.2	63.3 ⁽⁸⁾ 49.8 ⁽⁹⁾	*	*	Laminate showed good resin flow
PF-48A ⁽⁶⁾	D1516-36	0 ⁽⁵⁾	1250	275	23.3	1.85	30.3	67.4	47.5 ⁽⁹⁾	*	*	-
PF-48AR ⁽⁷⁾	D1516-36	0 ⁽⁵⁾	1250	275	26.2	1.82	27.6	71.3	49.7 ⁽⁹⁾	*	*	-
PF-49A ⁽⁶⁾	D1516-36	0 ⁽⁵⁾	1250	275-350	18.6	1.87	38.2	54.1	43.6 ⁽⁹⁾	*	*	-
PF-49AR ⁽⁷⁾	D1516-36	0 ⁽⁵⁾	1250	275-350	16.7	1.88	41.8	65.5	47.9 ⁽⁹⁾	*	*	-
PF-50A ⁽⁶⁾	D1516-36	0 ⁽⁵⁾	1250	275-425	19.6	1.73	46.4	46.2	33.8 ⁽⁹⁾	*	*	-
PF-50AR ⁽⁷⁾	D1516-36	0 ⁽⁵⁾	1250	275-425	21.6	1.79	38.3	64.5	42.9 ⁽⁹⁾	*	*	-
PF-51A ⁽⁶⁾	D1516-36	0 ⁽⁵⁾	1250	275-500	22.6	-	-	54.9	42.8 ⁽⁹⁾	*	*	Could not get voids and density due to blister
PF-51AR ⁽⁷⁾	D1516-36	0 ⁽⁵⁾	1250	275-500	24.4	1.72	38.4	61.4	33.2 ⁽⁹⁾	*	*	-

(7) Laminate was postcured to 600°F over 50 hours in argon

(8) After 1/2 hour at 400°F

(9) After 1/2 hour at 600°F

(10) After 1/2 hour at 700°F

* Data not available due to instrumentation difficulties

(1) All laminates were fabricated using style 181 "E" glass cloth with an A-1100 finish

(2) All laminates were of the BTDA-DAB-EG type resin with the exception of PF-45

(3) Laminate PF-45 was fabricated using PMDA-DAB-EG resin

(4) Prepreg conditioned for 45 minutes at 180°F in air

(5) Prepreg conditioned in a vacuum oven between 160-180°F

(6) Laminate was postcured to 600°F over 50 hours in air

Table VI. Summary of BTDA-DAB-EG and PMDA-DAB-EG Laminate Properties for Phase II Program

of four laminates was formed at maximum press temperatures of 250 and 275°F and a 1250 psi pressure. These laminates then were given a 50-hour postcure in argon to a maximum temperature of 600°F. Following these procedures decreased strengths below previous strength values, thus resins synthesized at high solids concentrations did not appear to produce improved laminates. The physical properties and strengths obtained for these four laminates are recorded in Table VII.

Tetraester Resins

A series of laminates was formed using resins prepared by reacting a previously prepared BTDA-EG ester with DAB. This resin was thought to contain BTDA which had been reacted to the tetraester form, thus all subsequent resins are referred to as tetraester resins. The details of the individual syntheses are documented in Section 3.2.

This series of laminates was formed using resins D1516-46 through D1516-51, with the exclusion of D1516-48, which was too viscous to treat in the same manner as the other more fluid resins. All of the five resins used to form these laminates were of the more fully esterified type. Early in the investigation it was found that these resins possessed much better flow characteristics than those BTDA-DAB-EG resins produced without water removal during the esterification process. A series of 2 x 2-inch test laminates were run using resin D1516-46 to determine the conditions necessary to minimize squeeze-out in the press during lamination.

As a result of this preliminary study, the drying of the prepregs was conducted at 225°F for either 25 or 15 minutes after each coat was applied to the glass cloth. The vacuum oven drying was discontinued and the prepregs were "B" staged for 5 minutes at 400°F prior to the laminating operation. Even with this more rigorous treatment of the prepregs it was found that long contact times at 450°F were necessary in the press to minimize resin squeeze-out. Since all but one of the five laminates delaminated in postcure, it appears that the laminates still contain a large amount of volatile material. This observation in conjunction with DTA data indicated that more vigorous

Laminate Designation (1) (2)	Resin Designation	Laminating Conditions			Final Resin Content, percent	Density, gm/cc	Volume Voids in Resin, percent	Average Flexural Strength (psi x 10 ⁻³)		Average Modulus (psi x 10 ⁻⁵)		Remarks
		Contact Time, minutes	Maximum Pressure, psi	Temp. Range, °F				Room Temp.	Elevated Temp.	Room Temp.	Elevated Temp.	
PF-52 ⁽⁷⁾	D1516-41	2 ⁽³⁾	1250	275	27.1	-	-	-	-	-	-	Specimen delaminated during postcure
PF-53 ⁽⁷⁾	D1516-42	3 ⁽³⁾	1250	275	27.8	1.73	31.2	58.7	52.4 ⁽⁹⁾ 43.7 ⁽¹⁰⁾	*	*	Laminate had a uniform appearance
PF-54 ⁽⁷⁾	D1516-41	2 ⁽³⁾	1250	250	20.2	1.83	37.0	56.5	52.5 ⁽⁹⁾ 42.2 ⁽¹⁰⁾	*	*	Laminate had a uniform appearance
PF-55 ⁽⁷⁾	D1516-42	3 ⁽³⁾	1250	250	24.2	1.74	36.4	42.7	38.5 ⁽⁹⁾ 30.4 ⁽¹⁰⁾	*	*	Laminate had a uniform appearance
PF-56 ⁽⁷⁾	D1516-46	6-1/2 ⁽⁵⁾	1250	450	25.3	-	-	-	-	-	-	Delaminated - could not cut specimens
PF-57 ⁽⁷⁾	D1516-47	5 ⁽⁵⁾	1250	450	28.2	-	-	-	-	-	-	Delaminated - could not cut specimens
PF-58 ⁽⁷⁾	D1516-49	5 ⁽⁵⁾	1250	450	24.0	-	-	-	-	-	-	Delaminated - could not cut specimens
PF-59 ⁽⁷⁾	D1516-50	5-1/2 ⁽⁵⁾	1250	450	21.5	-	-	-	-	-	-	Delaminated - could not cut specimens
PF-60 ⁽⁷⁾	D1516-51	5-1/2 ⁽⁵⁾	1250	450	18.2	1.84	40.6	51.3	49.5 ⁽⁹⁾ 39.2 ⁽¹⁰⁾	*	-	Laminate had a uniform appearance
PF-61 ⁽⁸⁾	D1516-53	1 ⁽⁵⁾	1250	500-700	23.7	1.84	29.3	58.9	50.6 ⁽¹⁰⁾	4.53	4.32 ⁽¹⁰⁾	-
PF-62 ⁽⁸⁾	D1516-53	4 ⁽⁵⁾	1250	400-650	18.0	1.93	33.5	72.4	56.8 ⁽¹⁰⁾	5.35	5.11 ⁽¹⁰⁾	-
PF-63 ⁽⁸⁾	D1516-53	3-1/2 ⁽⁶⁾	1250	400-650	25.6	1.86	24.1	70.2	56.1 ⁽¹⁰⁾	4.52	4.51 ⁽¹⁰⁾	-
PF-64 ⁽⁸⁾	D1516-55	4 ⁽⁴⁾	1250	400-600	23.4	1.78	34.8	52.3	52.5 ⁽¹⁰⁾	4.54	4.52 ⁽¹⁰⁾	-
PF-65 ⁽⁸⁾	D1516-53	-	15	350-450	17.8	1.56	59.2	63.8	52.8 ⁽¹⁰⁾	4.28	4.02 ⁽¹⁰⁾	Laminate formed by vacuum bag technique

(1) All laminates were fabricated using style 181 "E" glass cloth with an A-1100 finish

(2) All laminates were fabricated using BTDA-DAB-EG type resin

(3) Prepreg was conditioned in a vacuum oven at 180°F

(4) Prepreg was conditioned at 225°F and "B" staged at 300°F

(5) Prepreg was conditioned at 225°F and "B" staged at 400°F

(6) Prepreg was conditioned at 225°F and "B" staged at 500°F

(7) Laminate was postcured to 600°F over 50 hours in argon

(8) Laminate was postcured to 700°F over 17 hours in argon

(9) After 1/2 hour at 400°F

(10) After 1/2 hour at 600°F

* Data not available due to instrumentation difficulties

Table VII. Summary of BTDA-DAB-EG Laminate Properties for Phase II Program

drying and "B" staging of the prepreg as well as increased press temperatures would have to be used to eliminate the volatile material before postcure.

Table VII summarizes the behavior of laminates PF-56 through PF-60. Laminate PF-60 is described separately and in more detail in the following section since it is the only laminate from which specimens for flexural strength tests were successfully obtained in this section.

Laminates PF-56 through PF-59 were all prepared from pre-pregs which had been spatula coated with three coats of the respective resin with 15 minutes of drying at 225°F between each coating (with the exception of PF-56 which was dried 25 minutes at 225°F after each coating). The coated prepregs were then "B" staged at 400°F for 5 minutes and cut into 6 x 8-inch plies for laminating. All prepregs were prepared with style 181 glass cloth with an A1100 finish. All laminates consisted of 12 plies of the prepreg material.

PF-60.

Material. Style 181 glass cloth, A1100 finish BTDA-DAB-EG resin D1516-51 (23 percent solids).

Material Preparation: Three hand (spatula) coats were applied. Each coating was dried in a forced draft oven for 15 minutes at 225°F. The dried prepreg was "B" staged for 5 minutes at 400°F and then cut into 6 x 8 inch plies. The plies were very stiff and dry to the touch.

Molding: A 12-ply layup was placed in a press at 450°F with 5-1/2 minutes contact time. This relatively long contact time was necessary to prevent excessive resin squeeze-out. The pressure was increased to 1250 psi and held for 1 hour. The press was cooled to below 200°F, the pressure released and the laminate removed. This laminate was then postcured in argon by increasing the temperature from 275 to 600°F over a 48-hour period, held at 600°F for 2 hours, allowed to cool to below 200°F and removed from the argon atmosphere.

Observations: The laminate had a resin content (as molded) of 27.4 percent and a final (after postcure) resin content of 18.2 percent. The density of the finished laminate was 1.84 gm/cc and the volume percent voids in the resin was 40.6 percent. This laminate showed no visual evidence of delamination and test specimens were cut with no delamination occurring. However, the low final resin content and high volume percent voids in the resin tends to confirm the previous supposition that the properties of these last five laminates are due to the loss of a great amount of volatile material during the postcure cycle. The flexural strength test results also confirm that this was a mediocre laminate compared to some of those made previously and is not representative of those ultimate strengths that can be achieved by selecting the proper laminating procedures. The results of the flexural strength tests at room temperature, 400 and 600°F are recorded in Table VII.

Laminate PF-60 showed a relatively high flexural strength despite a low resin content and high volume percent voids in the resin. It was thought that resins prepared in a manner similar to that used to synthesize D1516-51 would be conducive to improve laminate formation if higher resin contents and lower voids could be achieved. The following section indicates that this reasoning is verified.

Resins Synthesized at Reflux Temperatures

Four laminates were formed using resins of the tetraester type which were reacted at reflux temperatures to the desired viscosity. The results obtained from this series of laminates are detailed in Table VII. This series of laminates indicated that laminates with flexural strengths above 70,000 psi and moduli on the order of 5×10^6 psi could be achieved with the tetraester type resins when the proper drying and "B" staging conditions were used. It appears that the optimum press temperatures for this type of resin is approximately 650°F. Since the tetraester type resins produced relatively high strengths with preliminary laminating studies, it is probable that these properties can be improved considerably by optimization of the

processing conditions. To ensure applicability of this type of resin to vacuum bag laminating techniques, a laminate was formed as described in the following section.

Vacuum Bag Layup

A laminate was formed using BTDA-DAB-EG tetraester type resin according to the conditions described in Table VII. This laminate was formed at a maximum temperature of 450°F with a subsequent postcure in argon to a maximum temperature of 700°F. This laminate had a flexural strength in the 60,000 psi range and a modulus above 4×10^6 psi. These strengths are very encouraging since they were achieved with a rather low resin content (17.8 percent) and a relatively high volume percent voids (59.2 percent). These results indicate that the tetraester type resin is conducive to laminating techniques that do not require high pressures, thus they should find uses in laminating processes where application of high pressures is not possible.

3.5 SPECIAL FABRICATION

To demonstrate the feasibility of forming a Pyrrone laminate in other than a flat shape, a piece of aluminum channel with inside dimensions of 1-1/8 inches wide by 7/16 inches deep was selected as a form. A prepreg was prepared that consisted of 181 glass cloth with an A1100 finish that had been coated with three coats of D1516-47 resin drying at 225°F for 15 minutes after each coating and then "B" staged at 300°F for 5 minutes.

The prepreg was cut into 2-1/4 x 5-inch plies and an 8-ply layup was formed in the aluminum channel using FEP Teflon both as a separator and as the vacuum bag material. One ply of perforated FEP Teflon was used on the outside of the part along with three plies of 181 bleeder cloth. The part was vacuum bagged and placed in an oven at 250°F, the temperature was increased to 450°F in 30 minutes, held at 450°F for 1 hour and cooled to below 200°F before removal from the vacuum bag and form.

The resin content of the part as it came out of the vacuum bag was calculated to be 24.2 percent. Then the part was cut crosswise into two separate parts of approximately the same size. One of these pieces designated PC-2 was placed in an argon postcure from 275 to 600°F in 48 hours, 2 hours at 600°F and removed below 200°F. The postcured part had a resin content of 19.6 percent, showed a slight amount of warping, had a very hard texture, was black in color and showed no evidence of delamination. The part which had not been postcured was designated PC-1, was packaged along with part PC-2 and shipped to NASA-Langley for examination.

A 4-ply laminate which had been made previous to PC-1 using the aluminum channel mold under the same conditions was found to have a resin content of approximately 28 percent. This piece was held at 750°F in air for 2 hours and found to have a resin content of approximately 20 percent.

3.6 LAMINATE WEIGHT LOSS

The flexural strength and modulus values obtained on laminates PF-61 through PF-65 at 600°F indicated that the resins currently being prepared possess reasonable high-temperature stability.

In an effort to better characterize the effects of resin preparation, resin content, volume percent voids, and curing conditions on the weight loss properties of these laminates, specimens of each of the five laminates were subjected to elevated temperature exposures in a muffle furnace. One specimen of each laminate in the "as molded" condition and one specimen of each laminate after postcure in argon were subjected to heating for periods of 1, 2, 3, and 4 hours at 750°F in air. The weight loss for each of the 10 specimens after the designated exposures are presented in Table VIII. It is interesting to note that in all cases the postcured sections of the five laminates showed the least weight loss up to 3 hours exposure at 750°F. However, after 4 hours the weight loss of all of the laminates except the one formed using the vacuum bag technique (PF-65) was greater for

Laminate Tested	Initial Weight, gms	Weight Loss, percent			
		After 1 Hour	After 2 Hours	After 3 Hours	After 4 Hours
PF-61 (as molded)	8.815	1.4	1.4	1.5	2.0
PF-61 (postcured)	8.971	0.5	0.8	1.3	3.5
PF-62 (as molded)	8.372	2.9	3.1	4.1	5.4
PF-62 (postcured)	8.121	1.3	2.1	3.7	5.5
PF-63 (as molded)	9.049	2.5	3.0	3.8	4.4
PF-63 (postcured)	8.878	1.6	2.5	3.9	4.7
PF-64 (as molded)	9.283	5.1	7.2	10.1	10.3
PF-64 (postcured)	8.657	2.0	3.5	7.2	11.3
PF-65 (as molded)	8.808	8.3	9.2	10.8	11.1
PF-65 (postcured)	8.263	2.1	3.1	5.4	7.5

Table VIII. Weight Loss of Pyrrone Laminates in Air at 750 F

the postcured condition than for the "as molded" condition. The reasons for this behavior are not clear, but it is thought that a combination of the void content, percent resin, and processing conditions contribute to this phenomenon.

3.7 MOLDINGS

In an attempt to determine the finished density of molded Pyrrone powders the precipitate obtained from varnish D1516-37 was used. The material was ground into a fine powder with a mortar and pestle and introduced into a 2-inch diameter mold. A pressure of 12,000 psi was applied and the temperature of the mold was varied from 300°F for 1 hour, 350°F for 1 hour to 400°F for 2 hours. The mold was cooled to below 200°F and the cast material removed. The finished molding had a density of 1.38 grams/cc and a Barcol hardness of approximately 50. Since it was shown that this diacid diester type of Pyrrone powder could be molded successfully an attempt was made to mold powder precipitated from the tetraester type

Two 1/2-inch diameter discs were pressed using D1516-46-2 precipitated Pyrrone powder. Both discs were pressed at 12,000 psi. One disk was held in the mold at 300°F for 1 hour and 450°F for 1 hour, allowed to cool to below 200°F and removed from the mold. This disk had a density of 1.36 gm/cc. The other disc was held in the mold at 450°F for 1 hour, allowed to cool below 200°F and removed from the mold. This disk had a density of 1.30 gm/cc.

3.8 FOAMS

Preliminary investigation indicated that the BTDA-DAB-EG Pyrrone resin will form a foam-like material by heating in air at 300°F. A sample of this type Pyrrone resin heated for 4 hours at 300°F formed a foam with a density of approximately 33 pounds per cubic foot. Subsequent postcuring of this foam from 275° to 600°F produced a hard, tough foam with a density of approximately 26 pounds per cubic foot.

3.9 DIFFERENTIAL THERMAL ANALYSIS

The DTA data for precipitated powders D1516-37 and D1516-46 are of much more interest than previous Pyrrone powders since there is a good indication that these materials undergo appreciable changes in very narrow temperature ranges.

The DTA data for powder D1516-37 indicate two endotherms, one at 138°C and another at 234°C. These are most probably associated with loss of volatiles such as residual solvent or condensation products. A broad gradual exotherm from 235°C on up into the 500°C temperature range is probably due to the curing reaction. It would appear that ultimate strength properties of this type Pyrrone will be achieved only if the final curing operation is conducted in the 400 - 500°C temperature range.

The DTA data for powder D1516-46 likewise indicate that final cure temperatures should be in the 400 - 500°C range to achieve the maximum degree of cure. This DTA data indicates that a very complex behavior is encountered in the curing mechanism of the powder derived from the more fully esterified BTDA-DAB-EG varnish. Three very sharp and intense endotherms are observed at 154, 211, and 297°C. These are most likely associated with the loss of volatile condensation products which are lost step-wise as the energy threshold of each discrete reaction is reached. It is probably molecularly held "solvent" which enhances the flow characteristics of these highly esterified varnishes and it could be expected that at temperatures just above each of these endotherms the flow characteristics will be lessened to some degree.

The DTA data aid in predicting optimum cure temperatures and thus eliminate a completely empirical approach to the optimization of processing conditions.

3.10 CONCLUSIONS

The most important conclusion of this program was that the resins prepared from the esters and the tetraamine in EG were useful for fabricating reinforced composite structures with excellent mechanical strength characteristics. Resins prepared from the dianhydride and the tetraamine in DMAc, on the other hand, failed to provide composites with adequate flexural strength.

Possible reasons for these results have been presented. Deleterious reactions of the polymer with the amide solvents were considered and cannot be excluded. However, the ionic nature of the A-A-A polymer formed in DMAc appeared to be a more important factor. Because of its ionic structure the A-A-A polymer is infusible, and lacking fusibility it does not undergo sufficient flow in processing to yield high-strength composites.

Polymerizations in EG were carried out with both the diester-diacid derivative and the tetraester derivative of the dianhydride. The structures of these esters were not established but were inferred from the methods of synthesis.

Theoretically, polymers derived from the diester-diacid should have the same fundamental structure as the ionic A-A-A polymers obtained in DMAc; nevertheless, they exhibited much better laminating characteristics. Two reasons may be given for the improved behavior in EG. First, the actual monomers were changed as well as the solvent, and this substantially decreased the rate and extent of reaction. The dianhydride is extremely reactive toward amines, and consequently high polymers are obtained at room temperature. DMAc also is a sufficiently strong solvent to retain these polymers in solution so that high molecular weights can be more readily achieved. A high molecular weight ordinarily would be desirable, but a combination of high molecular weight and ionic character makes the A-A-A polymer obtained in DMAc infusible. When the reaction is conducted in EG, the diester-diacid (which is the actual monomer) is far less reactive than the anhydride from which it was derived. Higher temperatures

are required to induce polymerization with the polymer precipitating from EG before high molecular weights are attained. Although an ionic A-A-A polymer may still be obtained, it probably has a relatively low molecular weight and consequently is still fusible. Polymerization ceases when the reaction mixture is cooled to room temperature. Therefore the A-A-A polymers obtained in EG probably are more desirable because they have lower molecular weights than similar polymers prepared in DMAc.

A second reason for the difference may be the EG or the EG-derived moieties which appeared to be bound to the A-A-A polymer. These moieties would have a plasticizing effect on the polymer and would promote flow.

An additional factor which should not be overlooked is that most of the polymers prepared in DMAc were PMDA-DAB polymers, while the polymers synthesized in EG were primarily BTDA-DAB materials. The additional single bonds of BTDA also should promote flow in processing.

Polymers prepared from DAB and the BTDA-EG tetraester were not ionic and, therefore, were readily fusible under processing conditions. If the sketchy analytical data are given credence, the actual structure of these polymers deviates considerably from the theoretical structure, but this does not detract from the performance of the cured materials.

The improved strength characteristics of laminates formed in Phase II of the program with BTDA-DAB-EG resins verified the expected improvement in flow characteristics. This increased flow which enabled the formation of higher quality laminates is primarily attributed to the internal bonding of the solvent (which acts as a plasticizer) and secondarily the increased molecular flexibility of the polymer formed from BTDA.

While the maximum room temperature flexural strength of Phase I laminates were on the order of 40,000 psi, it was found that room temperature flexural strengths above 70,000 psi could be routinely

achieved with the BTDA-DAB-EG resin system. The maximum moduli in Phase I were on the order of 3×10^6 psi while it was demonstrated that moduli above 5×10^6 psi could be achieved with the BTDA-DAB-EG resin system.

The high modulus may be of a great importance to the aerospace industry. In many design applications the stiffness of a material is of far greater importance than its ultimate strength.

It was observed that the volume percent voids in the resin of Phase I laminates were generally in the 40 to 60 percent range and the density of the laminates ranged between 1.46 and 1.82 gm/cc. These high voids and relatively low densities are attributed to loss of volatile components from the laminates during the curing procedure. In Phase II it was found that the increased strength properties were accompanied by a reduction in voids (generally in the 20 to 40 percent range) and increased densities in the 1.52 to 1.93 gm/cc range. These observations of void content and densities along with improved strengths indicate that increased flow characteristics have been achieved while the effects of the loss of volatile components have been minimized.

The effect of postcuring the BTDA-DAB-EG laminates in air and argon indicates that better strengths are achieved in all cases with the argon postcure.

A vacuum bag layup utilizing the BTDA-DAB-EG resin system demonstrated that flexural strengths above 60,000 psi and a modulus above 4×10^6 psi could be achieved utilizing this technique.

4.0 REFERENCES

1. Anon. , Chem. Eng. News, 43, 38 (May 17, 1965).
2. V. L. Bell and G. F. Pezdirtz, Polymer Preprints, 6, No. 2, 747 (1965).
3. V. L. Bell and G. F. Pezdirtz, J. Polymer Sci. , B3, 977 (1965).
4. V. L. Bell and R. A. Jewell, Polymer Preprints, 8, No. 1, 235 (1967).
5. F. Dawans and C. S. Marvel, J. Polymer Sci. , A3, 3549 (1965).
6. J. G. Colson, R. H. Michel and R. M. Paufler, J. Polymer Sci. , 4A-1, 59 (1966).
7. M. M. Tessler, Polymer Preprints, 8, No. 1, 152 (1967)
8. R. L. Van Deusen, J. Polymer Sci. , B4, 211 (1966).
9. R. L. Van Deusen, O.K. Goins and A. J. Sicree, "The Formation and Properties of a Class of Highly Condensed Aromatic-Heterocyclic Polymers," AFML-TR-66-373, February 1967.
10. Ham and Beindorff, U. S. 2,811,548 (1957).